2007

Concentration and extraction of phosphorus from swine manure slurries as struvite

Timothy Allen Shepherd
Iowa State University

Concentration and extraction of phosphorus from swine manure slurries as struvite

by

Timothy Allen Shepherd

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Agricultural Engineering

Program of Study Committee:
Robert T. Burns, Major Professor
D. Raj Raman
Kenneth J. Stalder

Iowa State University

Ames, Iowa

2007

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Acknowledgments

I would like to thank everyone who has allowed me to be successful during my undergraduate and graduate career through their constant mentoring, encouragement, and assistance. I especially appreciate the efforts and enthusiasm of my committee members Drs. Robert Burns, Raj Raman, and Ken Stalder, who provided me with the direction, advice, feedback, and most importantly encouragement which allowed me to succeed in my efforts.

I have had the privilege of working with and learning from the very best in the business. Dr. Burns has provided me with unforgettable and invaluable experiences and opportunities in all aspects of my study, well beyond the scope of my research. I hope that I can instill his dedication, motivation, and work ethic into my career. I would like to thank Lara Moody and Dr. Raman for there support in all of my efforts.

I owe my most sincere gratitude to the never-ending list of the Animal Waste Management Team members who assisted with my research, tolerated my eccentricities, and most likely went home smelling quite ripe. My many thanks go to: Ross Muhlbauer, Wei Wu-Haan, Lara Pepple, Dan Anderson, Hong Li, Brian Zelle, Carl Peterson, Ember Muhlbauer, Jay Duncan, Gayle Bishop, Randy Swetka, Neil Heithoff, Lana Meyer, Katie Heathcote, and Todor “The Disagreer” Mitev (I am sure I missed one of you; if so, I will print a special copy with your name inserted in red ink).

Last, but not least, I would like to thank my family and friends for their unconditional support and encouragement in all aspects of my life.

CHAPTER 1

GENERAL INTRODUCTION

Introduction

Manure generated in modern pork production facilities is typically land-applied as a fertilizer for crop production. The consolidation of animal production in recent years has created localized concentrations of nutrients such as nitrogen, phosphorus, and potassium (Zhu et al., 2001). When applying manure slurries at levels to only meet the crop requirements for nitrogen, phosphorus can be over-applied leading to accumulation of phosphorus. The over-application of phosphorus fertilizers, manure or commercial, on agricultural fields has been recognized as a surface water quality threat in Europe and the United States (Greaves et al., 1999).

Water quality and land management concerns have resulted in new requirements for the land application of manure slurries. These requirements frequently appear as regulations to limit the application of manure slurries based on crop macronutrient needs, such as nitrogen or phosphorus (Shober and Simms, 2003). In many cases, the maximum allowable slurry application rate is limited by the phosphorus content of the slurry. Phosphorus based manure application rates can require up to eight times the land needed for nitrogen based application rates (Burns et al., 1998). In addition to larger land requirements needed for phosphorus based applications rates, application of supplemental nitrogen may be needed for optimal crop production.

To alleviate the local concentration of nutrients, comply with nutrient application regulations, and reduce the risk of over-applying phosphorus to agricultural fields, a treatment system capable of economically removing phosphorus prior to land application is needed.

Objectives

The objective of this research was to address the application of dedicated struvite reactors for full-scale pork production operations by:

1) Investigating a method that quickly identifies maximum struvite precipitation, accounting for real-time variations of magnesium demand within the manure slurries.

2) Developing and testing a short-retention-time pilot-scale reactor that:

a) Effectively and reliably reduces DRP in a variety of swine manure slurries

b) Provides separation and recovery of precipitated struvite for TP reduction

c) Can be effectively applied to modern pork production systems across a variety of manure management systems

Thesis Organization

The research presented in this thesis is comprised of three papers, each corresponding to specific research objectives. The first paper entitled “Investigation of a Magnesium Injection System to Determine Amendment Requirements for Phosphate Precipitation” will be submitted to *Applied Engineering in Agriculture*. The second paper entitled “Development of a Bench-Scale Air Sparged Continuous Flow Reactor for Struvite Precipitation from Two Different Liquid Swine Manure Storage Systems” has been submitted to *Biosystems Engineering*. The third paper entitled “Performance of a Pilot-Scale Air Sparged Continuous Flow Reactor and Hydrocyclone for Struvite Precipitation and Removal from Liquid Swine Manure” will be submitted to the *Transactions of the ASABE*.

Literature Review

Contemporary wastewater treatment systems commonly use metal and polymer precipitation or flocculation to remove phosphorus, creating an unusable phosphorus side stream which is discarded landfilled (de-Bashan and Bashan, 2004). Ideally, a treatment system would provide phosphorus removal while simultaneously producing a reusable phosphorus byproduct. Evaluation of phosphorus removal technologies should identify traditional measures such as capitol and operational costs, degree of treatment, efficiency, and feasibility of application, but should also value sustainability and utilization of phosphorus byproducts.

Emerging phosphorus removal technologies which create a usable phosphorus byproduct vary widely and incorporate biological, chemical, and physical methods. Examples of biological methods for phosphorus removal include wetlands, enhanced biological phosphorus removal (EBPR), and microalgae suspensions. Biological treatment can provide significant phosphorus reductions; however, they generally operate at low efficiencies (Battistoni et al., 2002). Incorporating a biological phosphorus removal technology on-farm may require long treatment times to overcome low efficiencies, necessitating large reactors and increasing the associated capital costs. Furthermore, most biological treatment processes are sensitive to, concentrated, high-strength wastes and fail if overloaded. Manure slurries are generally considered to be of high-strength and require dilution or pre-treatment to avoid overloading a biological phosphorus removal system.

Forced precipitation of dissolved reactive phosphorus (DRP) as struvite is a chemical phosphorus removal technology. Precipitation of struvite can significantly reduce the amount of DRP in manure slurries, while simultaneously allowing for the concentration of phosphorus for recovery and future use (Bowers and Westerman, 2005a; Burns et al., 2001; Munch and Barr, 2001; Ohlinger et al., 2000). In laboratory and field tests, forced struvite precipitation has been shown to remove 90% or more of the DRP from swine manure slurry (Burns et al., 2001).

If a sufficient fraction of total phosphorus (TP) is available as DRP, struvite precipitation can provide significant reductions of TP in swine manure slurries. Controlling the amount of phosphorus removed during treatment can allow adjustment of nitrogen to phosphorus ratios, providing the potential to balance N and

P to match crop requirements. Additionally, recovered struvite can be used as a slow-release commercial or agricultural fertilizer, offering potential as an added value byproduct (de-Bashan and Bashan, 2004).

Currently, there are several treatment systems that apply struvite precipitation techniques for phosphorus removal in municipal and industrial wastewaters (Munch and Barr, 2001; Ohlinger et al., 2000). Full-scale struvite reactors have been incorporated into municipal and industrial wastewater treatment systems in Japan and Europe, but their implementation is not a common practice in livestock production facilities (Burns et al., 2003). Dedicated struvite reactors and treatment methods have been developed at bench and pilot-scale for agricultural wastewater treatment, generally focusing on batch reactions and continuous flow fluidized bed processes at low flow rates (Burns et al., 2001; Bowers and Westerman, 2005b). However, current research has not sufficiently addressed the application of dedicated struvite reactors for full-scale pork production operations.

Principles of Struvite Precipitation

Struvite is a crystalline precipitate technically described as magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4*6H_2O$). To form struvite magnesium, ammonium, and phosphate ions must be available in sufficient concentration to provide an adequate precipitation potential. In a pure solution, a 1:1:1 (Mg^{2+}: NH_4^+:PO_4^{3-}) molar ratio can form struvite; if any one constituent is not available, struvite will not form. Optimization of struvite precipitation is also influenced by pH and reaction time.

Struvite Formation

The rate of struvite formation depends upon the conditional solubility product (K_{sp}) of struvite which is directly proportional to the product of Mg^{2+}, NH_4^+, and PO_4^{3-} ions in solution. The precipitation potential of struvite is highly dependant on K_{sp} and solution pH; as pH increases, the dissolution/precipitation equilibrium curve for struvite decreases allowing a greater degree of struvite precipitation to occur (Ohlinger et al., 2000).

Struvite precipitation can occur via two distinct pathways: crystal growth and nucleation. Studies by Ohlinger et al. (2000) and Nelson et al. (2003) identified that struvite kinetics of crystal growth followed first order kinetics with rate constants ranging from 4.2 to 12.3 h^{-1}, depending on the solution pH. Turker and Celen (2007) reported that the struvite nucleation followed second order kinetics. Nucleation has a significantly faster kinetic rate than crystal growth, indicating that implementation of a struvite precipitation reactor promoting nucleation can reduce hydraulic retention required in comparison to reactors utilizing crystal growth.

Hydraulic Retention Time

A hydraulic retention time (HRT) of 10 minutes has been shown to be more than sufficient to form struvite in swine manures (Burns et al., 2003). Furthermore, experiments by Burns et al. (2003) have shown that a 40-minute HRT removes only 4% more DRP when compared to a 10-minute HRT. Hydraulic retention time determination is economically relevant to reactor design and sizing, shorter HRT's allow for a minimum tank size while maintaining relatively equal phosphorus removal

rates. Additionally, increasing the reaction time increases the possibility of magnesium and phosphorus complexation, creating unwanted precipitants such as brushite, monetite, and dolomite (Celen et al., 2007).

pH Adjustment

Struvite precipitation is significantly influenced by the solution pH. Struvite formation increases with pH until it reaches its maximum precipitation point near a pH level of 9.0 (Buchanan et al., 1992). Consideration of chemical and energy costs should be accounted for when determining the level of pH adjustment. The system should provide economically feasible treatment while maintaining appropriate phosphorus removal rates. Furthermore, increasing pH also increases volatilization of ammonia, and excessive pH increases should be avoided. Two methods to increase pH in swine manures are chemical amendment with a caustic material such as sodium hydroxide, or carbon dioxide (CO_2) removal via mechanical aeration utilizing either air sparging or agitation.

Caustic amendment provides a rapid pH increase with low energy costs; however, treating manure slurries on farm would require a large amount of caustic material. Material cost and on-farm storage of a caustic make this method of increasing pH prohibitive.

Air sparging and agitation offer an alternative to caustic amendment for pH adjustment. Mechanical aeration methods increase pH through CO_2 stripping and subsequent reduction of carbonic acid levels in the manure. Manure slurries with high alkalinity levels reduce the efficiency of aeration for pH adjustment. Power consumption and required time to achieve the desired pH adjustment may limit the

application of aeration in continuous flow struvite reactors. Ohlinger et al. (2000) used a two-stage pH adjustment tank prior to a struvite reactor; air sparging was implemented for primary pH adjustment and sodium hydroxide provided supplemental adjustment when aeration was not capable of maintaining the desired pH.

Agitation is often necessary to mix the layers within an on-farm liquid storage system to provide uniform nutrient loading during field application. Agitation could be utilized and monitored to increase the slurry to acceptable pH levels prior to entry into the struvite reactor, reducing system cost. Research on low-level aeration (1 L/min) of manure slurries indicated that the pH of manure can be raised approximately one unit in one day (Zhu et al., 2001).

Determination of Magnesium Requirements

In typical manure slurries, Mg^{2+} is the limiting ion for optimized struvite formation; this requires the addition of magnesium to maximize DRP removal. In a pure solution, a 1:1:1 (Mg^{2+}: NH_4^+:PO_4^{3-}) molar ratio will form struvite. However, in heterogeneous organic solutions such as manures, magnesium can form complexes with other ions in solution, reducing magnesium's net contribution to the K_{sp} of struvite. To overcome competing reactions and achieve the desired DRP removal rates, magnesium may be required at levels higher than the stoichiometric requirement (Burns et al., 2003).

Determining appropriate injection rates of magnesium is paramount in the optimized precipitation of struvite. Different manures will require different amounts of

magnesium injection and pH amendment, therefore a method of determining or predicting the magnesium demand for the desired struvite formation is essential for manure treatment applications. Several approaches for struvite precipitation in manure slurries have been developed and utilize varying methods to determine the required chemical amendment. A feasible farm-scale system should be capable of determining the amendment rates for variable conditions in real-time with robust equipment while maintaining low initial investment.

Bowers and Westerman (2005a) suggest injection rates for ammonia and magnesium based on laboratory analysis of the initial phosphorus, nitrogen, and magnesium amounts of typical manure slurry. Bowers and Westerman (2005a) also indicated that in some cases phosphorus removal exceeded theoretical predictions based on the initial slurry conditions. Using a single lab analysis does not account for changes in manure characteristics that are likely to occur during a land application event lasting several hours. Amendment additions based only on initial laboratory tests may cause excess chemical cost or decreased struvite precipitation under variable conditions.

An optimization study of struvite precipitation in swine manure conducted by Burns et al. (2003) determined that a molar ratio of Mg^{2+}:PO_4^{3-} of 1.6:1 was the most effective amendment amount for various swine manures. This molar ratio accounts for magnesium complexing, however, it was derived from a limited number of swine manures with specific manure management practices, and may not be applicable to other swine operations or animal species. Furthermore, experiments were conducted in batch reactions and the molar ratio was determined from initial

conditions of the manure slurry. The excess ratio of Mg^{2+} allows for competing reactions, but does not account for changes in the manure slurry during continuous flow operation.

Ohlinger et al., (2000) investigated struvite removal in municipal wastewater treatment and calculated the amendment needs for a continuous flow reactor based on kinetic rate constants determined in batch experiments. Munch and Barr (2001) tested a pilot system based on the Phosnix process developed by Unitika Ltd. The Phosnix process sets magnesium injection to provide a Mg:P ratio of 1.3:1. Municipal waste is generally less variable than manures from various livestock operations, allowing steady-state assumptions to be more realistic. During land application, pump-out disrupts settled solids and changes nutrient concentrations within the manure slurry. Manure slurries may violate assumptions steady-state conditions and constant reaction rates.

Utilization of automated analysis equipment such as atomic absorption instruments for magnesium and colorimetric instruments for phosphorus would allow a user to update the slurry conditions as the treatment proceeds. Implementing automated analysis systems such as these on a farm-scale system is likely not economically feasible at present due to the relatively high equipment cost. Furthermore, due to high solids content and the corrosive nature of manure slurries, the robustness of automated analysis systems may be an issue.

Modeling struvite formation is also possible by utilizing Visual MINTEQ. Visual MINTEQ models chemical equilibrium by utilizing a defined thermodynamic database. Ali et al., (2003) evaluated struvite precipitation potential with Visual

MINTEQAE version 4.0, simulating batch reactions to create a large database of struvite precipitation potentials for application to struvite reactors. The MINTEQ program allows the user to identify complexing reactions with magnesium and phosphate ions. Accurate predictions of the complexing reactions require the user to define a large array of ions present in the manure slurry, including but not limited to Mg^{2+}, PO_4^{3-}, NH_4^+, Ca^{2+}, K^+, and alkalinity (Celen et al., 2007). The use of MINTEQ modeling to determine reaction characteristics is based on initial conditions and does not account for changes in manure slurry that may occur during a land application event. Application of MINTEQ modeling to determine real-time magnesium demand would require the continuous monitoring of interacting ion concentrations, which may not be technically or economically feasible at the present time.

Magnesium Sources

Several chemicals can be utilized for phosphate removal in wastewaters. The most common include lime, ferric metals, magnesium hydroxide ($Mg(OH)_2$), magnesium oxide (MgO), and magnesium chloride ($MgCl_2$). Adding lime or ferric metals does not precipitate struvite; however they do complex with phosphate to from precipitants. Magnesium hydroxide, MgO, and $MgCl_2$ are all viable magnesium sources to force struvite formation.

Magnesium hydroxide and MgO have low solubility characteristics and would require a water slaking system similar to lime softening systems for effective implementation. Without dissolving in a water slacking system prior to amendment, the reaction times required for struvite precipitation would be significantly increased

due to the low solubility of $Mg(OH)_2$ and MgO, 0.0012 g/100g H_20 and 0.00062 g/ 100g H_20, respectively. Slaking systems are difficult to operate with consistency and can create issues with amendment accuracy. Miles and Ellis (2001) utilized $Mg(OH)_2$ and MgO to force precipitation; however, the low solubility and precipitation potential of $Mg(OH)_2$ prior to amendment reduced amendment accuracy. Magnesium hydroxide and MgO both increase solution pH, reducing the pH adjustment requirement for optimized struvite precipitation.

Magnesium chloride has a high solubility, 54.2 g/100g H_20, which makes it easier to handle and reduces the required reaction time in comparison to $Mg(OH)_2$ and MgO (Burns et al., 2001). However, $MgCl_2$ is acidic and does not provide the added benefit of increasing the pH of the manure slurry, requiring greater pH adjustment to optimize struvite precipitation. For agricultural applications, the use of $MgCl_2$ can reduce equipment cost and labor while increasing the accuracy of dosing when compared to the use of less soluble magnesium compounds.

Application of Struvite Precipitation in Pork Production Facilities

The most important design parameter of a struvite reactor is its ability to function at field-scale within existing pork production systems. Pork production facilities and their manure management systems vary significantly, requiring a flexible design. A flexible system requires an easily modifiable design that can accommodate differences between manure management strategies and manure characteristics from different liquid manure storage systems involving a variety of livestock species.

Point of treatment

Determining the most appropriate, feasible, and cost effective implementation point for manure slurry treatment sets the design criteria for a viable struvite precipitation systems and phosphorus removal. For reaction and energy input efficiency, the optimal time for implementing a continuous flow struvite reactor is during the agitation of stored manure prior to, and in series with, land application events. Agitation provides a homogenous manure mixture and has the potential to increase manure slurry pH via CO_2 stripping; reducing chemical and energy costs associated with pH adjustment.

The most common manure slurry storage systems utilized in pork production include under floor deep-pit confinements, storage tanks, holding ponds, and anaerobic lagoons. A nutrient removal system could be designed to treat manure over an extended period at low flow rates. However, this strategy necessitates a post-treatment storage system, increasing capital expenditures. Implementing a treatment system in series with field application events requires higher treatment flow rates, but reduces the need for a post-treatment storage system.

Deep-pit manure storage systems require specific management practices to minimize the concentration of hydrogen sulfide gas (H_2S) inside the production facility. To avoid increasing the amount of H_2S released from the stored manure slurry, agitation is avoided except during field application events. To minimize H_2S risk in deep-pit storage facilities, the most feasible treatment scheme requires a system capable of treatment during land application events.

Manure slurry treatment systems that can perform at relatively high flow rates under variable environmental conditions are desirable for implementation within existing swine production systems. During land application events, manure slurry is typically applied at rates ranging from 2300 to 6800 L/min (~500 to 1500 gpm). This high volume application rate requires a treatment system with comparable flow rates, necessitating short retention times to avoid excessively large reactors.

The majority of struvite research has focused on in-situ struvite precipitation or bench and pilot-scale reactors operating at low flow rates. Bowers and Westerman (2005b) tested a field-scale fluidized bed struvite reactor which treated manure slurries at 5.6 and 9.5 L/min (1.5 and 2.5 gpm). Munch and Barr (2001) tested a bench-scale fluidized bed reactor which treated waste water ranging from 0.3 to 2 L/min. Modifications to achieve high flow rates required to make fluidized bed reactors applicable for use with large modern pork production operations may not be economically feasible.

In-situ Struvite Precipitation

Laboratory and field scale experiments by Burns et al. 2001 investigated the application of in-situ lagoon struvite precipitation for phosphorus removal from swine manure slurries. Utilizing in-situ lagoon struvite precipitation can provide significant phosphorus reductions prior to land application events. However, precipitated struvite settles to the bottom of the lagoon, and does not readily allow for the recovery of precipitated struvite.

Fluidized bed reactors

Fluidized bed reactors are designed to provide optimal conditions of struvite precipitation onto bed particles via crystal growth. Bowers and Westerman (2005a) developed a cone-shaped fluidized bed reactor for treatment of swine wastewater. Their system utilized a fluidized bed containing struvite to promote the growth of struvite crystals within the reactor. Modeling and testing indicated that the conical reactor created plug-flow conditions for the liquid and provided a completely mixed fluidized bed. Complete mixing of the bed indicates that there is significant vertical mixing of bed particles creating a uniform distribution of particle sizes throughout the bed, as compared to a perfect classification of a fluidized bed which indicates that bed particles are stratified with respect to their size and density. Field tests provided removal rates of dissolved reactive phosphorus (DRP) ranging from 13% to 80%, and total phosphorus (TP) removal rates ranging from 0% to 80%. Under certain operating conditions, testing provided evidence of spontaneous nucleation and seeding. Spontaneous nucleation and seeding decreased the bed particle size and reduced phosphate removal performance due to struvite becoming entrained with the effluent and wash out of the reactor. Bowers and Westerman (2005b) reduced the flow rate through the reactor to maintain struvite settling in order to ensure that struvite and bed washout did not occur.

Munch and Barr (2001) modeled and tested a pilot-scale fluidized bed struvite reactor based on the Phosnix process developed by Unitika Ltd (Japan) (Brett et al. 1997). Munch and Barr's (2001) reactor utilized a struvite seed material to develop the fluidized bed and promote further precipitation upon the surface of the bed

material. They used a municipal wastewater with low TS conditions, achieving a DRP removal rate of 94%. Fine struvite crystals were found in the effluent of the reactor, accounting for lower than expected TP removal rates. If struvite precipitates via nucleation and not as crystal growth in a fluidized bed reactor, the upflow velocity within the system may be great enough to push small struvite particles out of the reactor, reducing the overall phosphorus removal performance.

With the inconsistent nature of agricultural wastewaters, a rapid increase in TS of the influent manure has the potential to create a similar washout effect in fluidized bed reactors and thus, provide lower than expected phosphorus removal rates. Additionally, organic matter and other suspended particles could interfere with the struvite bed particles and reduce the precipitation potential of struvite onto the bed particles. Spontaneous nucleation of fine struvite particles in a fluidized bed reactor can become entrained in the effluent, reducing TP removal performance. Fluidized bed reactors are complex in design, fabrication, and operation. Bench and pilot-scale fluidized designs have provided significant phosphorus removal efficiencies (Bowers and Westerman 2005ab, Munch and Barr 2001). The adoption of full-scale fluidized bed reactors to on-farm systems may be limited because of their complexity; furthermore, modifications to achieve high flow rates required to make this type of system applicable for use with large modern pork production operations may not be economically feasible.

Continuous Flow Stirred Tank Reactor

A continuous flow stirred tank reactor (CSTR) can provide a platform capable of creating optimal conditions and sufficient reaction times for struvite precipitation. Continuous flow stirred tank reactors inherently buffer shock loading (Benfield and Randall, 1987); thus, the phosphorus removal efficiency will be less susceptible to changes in the manure slurries, providing a robust system. Furthermore, CSTRs are relatively simple in design, and their sizing is well defined (AWWA, 1999). The simple design parameters also provide operational and maintenance benefits associated with startup and process changes that may not be available with fluidized bed reactors. However, CSTR's do not provide a mechanism for struvite separation for the overall goal of TP reduction.

Achieving TP reduction with a CSTR requires a downstream separation system for struvite-based phosphorus removal. Struvite has a specific gravity of 1.7, while liquid swine manure has a specific gravity near 1.0; this difference should permit gravity or centrifugal separation for the ultimate removal and recovery of precipitated phosphorus from the manure slurry.

A post-treatment settling basin would allow precipitated struvite to be removed from the manure slurry. If large volumes of manure slurry are treated during a land application event, the size of a settling basin required may not be physically available or economically viable. Furthermore, a settling basin may not readily allow for the recovery of precipitated struvite.

Up-flow clarifiers (UFCs) are commonly used in municipal wastewater treatment systems to separate solids from liquids in continuous flow systems

(AWWA, 1999). They are designed to reduce the up-flow velocity of the liquid to allow for the gravitational settling in a continuous flow process. Typically, UFCs are used to remove grit, suspended solids, and flocculated particles. UFC's are designed to remove material with a specific size and density. The high specific gravity struvite allows for a UFC to be designed to remove struvite particles of a certain size. The use of gravitational settling allows for UFCs to maintain low operating costs, while achieving continuous flow solids separation. Up-flow clarifiers, like fluidized bed reactors, may have reduced TP removal rates if small struvite particles are present.

Separation with a centrifuge or hydrocyclone provides an alternative, continuous-flow, method for struvite recovery. Centrifuges and hydrocyclones created centripetal acceleration which imparts a perpendicular force onto materials in a liquid or gas. The perpendicular force, commonly called gravities due to acceleration, allow for the separation of materials based on differences in density. Separation with centrifuges and hydrocyclones follows the principles of sedimentation; by increasing the gravitational force applied separation is enhanced. Continuous flow centrifuges are utilized in industrial process like ethanol production, however their implementation in on-farm systems is cost prohibitive under current conditions.

Hydrocyclones have no moving parts and have considerably simpler designs than centrifuges. A hydrocyclone is designed to force fluid flow in a tangential path around a cylinder or cone, creating centripetal acceleration. They can select for

particles of the same density but different sizes; or in the case of fine particles, select for higher density particles. Larger and denser materials are forced to the outside wall where they collected at the bottom of the hydrocyclone, while less dense materials remain on the inside. A hydrocyclone has two effluent streams, the underflow consists of high specific gravity materials large enough to reach the wall and some entrained liquid, the overflow consists of the low density liquids and particles too small for separation.

Hydrocyclones are most commonly used to separate particulate matter from air, gas from liquids, solids from liquids, or high density liquids from low density liquids. Hydrocyclone technology has also been implemented in dairy manure management systems for the removal of fine sand particles from manure slurries. The high gravitational forces generated within a hydrocyclone increase the removal potential of small struvite particles when compared to traditional settling basins and UFCs, and may provide a simple method to recover struvite and reduce TP.

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CHAPTER 2

USING CONDUCTIVITY TO PREDICT MAGNESIUM ADDITION REQUIREMENTS FOR STRUVITE PRECIPITATION IN SWINE MANURE SLURRIES

To be submitted to *Applied Engineering in Agriculture* for publication

Timothy A. Shepherd, Robert T. Burns, Lara B. Moody, D. Raj Raman, Kenneth J. Stalder

Abstract

The goal of this project was to develop a system that identified magnesium demand for struvite formation by monitoring conductivity changes during continuous injection of magnesium chloride in several different manure slurries. The conductivity of six manure slurries was monitored to identify the response due to magnesium chloride injection and struvite precipitation. Struvite precipitation is a technically feasible treatment method for phosphorus removal and recovery from manure slurries (Bowers and Westerman, 2005a; Burns et al., 2000). Swine manure slurries typically require the addition of magnesium (Mg^{2+}) to force struvite precipitation. The quantity of Mg^{2+} required for maximized phosphorus removal is generally determined through laboratory tests. Optimized struvite precipitation in a field setting would require a real-time method to determine Mg^{2+} addition rates for the duration of a land application event. This paper will discuss the requirements of a feasible automated control system which monitors and controls the injection of Mg^{2+} to force struvite precipitation, accounting for real-time variations of magnesium demand. Theoretical predictions and pure solution tests provided information capable of determining the magnesium demand for struvite precipitations. After testing six different manures in

triplicate, the conductivity responses did not follow theoretical predictions and failed to provide any indication of optimum magnesium injection rates for phosphorus removal.

Keywords: Manure, Phosphorus, Struvite, Magnesium Chloride

Introduction

Struvite is a crystalline precipitate technically described as magnesium ammonia phosphate hexahydrate ($MgNH_4PO_4*6H_2O$). To form struvite, magnesium, ammonia, and phosphate must be available in an ionic form to provide an adequate precipitation potential. Magnesium is the limiting ion in typical manure slurries, requiring the addition to force struvite formation. In a pure solution, a 1:1:1 (Mg^{2+}: NH_4^+:PO_4^{3-}) molar ratio will form struvite. In complex organic solutions, such as manures, this ratio may not be adequate, requiring higher that stoichiometric magnesium additions to overcome complexing reactions (Burns et al., 2003). The objective of this project was to develop a method that quickly identifies maximum struvite precipitation in manure slurries, allowing for real-time determinations of magnesium demand.

Determining appropriate injection rates of magnesium is paramount in the optimized precipitation of struvite. Variability within and across manure slurries require different amounts of magnesium injection and pH amendment. Furthermore, during land application events, pump-out disrupts settled solids and changes ion concentrations within the manure slurry. Current methods used to determine magnesium demand rely upon initial analysis of manure slurries and do not account for changes in a manure slurry that may occur during a land application event. A

feasible farm-scale system should be capable of determining the real-time magnesium amendment rates under variable conditions with robust equipment for a reasonable initial investment.

The development of an automated feedback control system for magnesium amendment would allow a struvite reactor to account for variations within manure slurries and across different manure handling systems. A flow injection analysis (FIA) approach may provide information that allows for the determination of the struvite precipitation potential and degree of constituent ion availability for further struvite formation. Ion selective electrodes (ISE) are the workhorses of FIA systems and can be used in direct sensing of analyte ion activities or sensing the activities of reagent ions after reaction with analytes (Coetzee and Gardner 1986). Monitoring Mg^{2+}, NH_4^+, or PO_4^{3-} ion activity with an ISE would allow for direct measurement of the struvite reaction. Speciation modeling with MINTEQ indicates that a magnesium ISE could be used to infer struvite supersaturating (Ali et al 2003).

Magnesium ISE sensors can be found for applications in molten metal processing (Fergus, 2000) and for biological fluids such as blood (Zhang, 2006). However, no appropriate magnesium-specific ISEs are available for application in a manure system. Ammonia and ammonium ISEs are commercially available and have been thoroughly investigated. Problems with fouling and drift in manure solutions decrease the reliability of using ammonia ISE to monitor the struvite reaction in manure slurries(Winkler et al., 2004). Also, the solubility of ammonia and ammonium is dependant on solution pH. The ideal operating point for struvite precipitation is 8.5-9.0; at this point the concentration of ammonium is highly

sensitive to changes in solution pH. A change in solution pH will affect the ISE output, and may provide false information pertaining to the struvite reaction. Phosphate ISEs have been implemented to monitor soil macronutrients in real-time (Kim, 2006), however literature and product searches did not find a wastewater application of phosphate ISE's.

Theory

Monitoring conductivity in a solution during struvite reaction could possibly provide information indicating reaction completion and magnesium demand. Specific conductance, K (S/cm), commonly used to determine the total dissolved solid content of a solution, is a direct measure of ions in solution. Conductivity varies with the type and number of ions in solution. As struvite precipitates out of solution, conductivity will change dependant upon the amendment procedure and reaction state. Specific conductivity, κ, can be calculated from the following fundamental relationship show in Equation 2.1.

Equation 2.1 $$\kappa = \frac{\Lambda \times N}{1000}$$

where: N = Normality of the solution (eq L^{-1})

Λ = equivalent conductance of the solution (S m^2 mol^{-1})

Equivalent conductance of the solultion, Λ, is calculated by the summation of the equivalent ionic conductance of each species in solution, λ_o, Equation 2.2. Table 2.1 provides a list of equivalent ionic conductance for species of interest in this system.

Equation 2.2 $$\Lambda_0 = \lambda_0^+ + \lambda_0^-$$

Table 2.1. Equivalent Ionic Conductivities (Infinite Dilution at 25°C)

Ion	λ_o (10^{-4} S m^2 mol^{-1})
1/2 PO_4^{3-}	69.0
NH_4^+	73.5
1/2 Mg^{2+}	53.0
Cl^-	76.3
Na^+	50.1
OH^-	198
H^+	349.6

(CRC 1990)

For a simple system, the addition of $MgCl_2$ in distilled water will have the predicted conductivity shown in Equation 2.3.

Equation 2.3 $$\kappa = \left[Mg^{2+}\right]\lambda_0^{Mg2+} + \left[Cl^-\right]\lambda_0^{Cl-}$$

For a more complex system, where multiple species are present, this relationship shown in Equation 2.3 extends. As magnesium chloride is added to a solution with available phosphate and ammonium, struvite may precipitate. As struvite precipitates under these conditions the concentration of available ammonium and phosphate ions are reduced while chloride ions are added, creating a small net gain in specific conductivity. If magnesium chloride addition exceeds the molar ratio of ammonium or phosphate, no additional struvite precipitates, theoretically increasing the conductivity. Monitoring the rate of conductivity change during

magnesium chloride injection for struvite precipitation may allow for the identification of maximum struvite precipitation.

Materials and Methods

Three experiments were performed to validate theoretical predictions of conductivity response to magnesium amendment in pure solutions. One experiment was designed to determine the applicability of conductivity response in swine manure slurries. All experiments used well-mixed 1.5 L sample volumes in 2.5 L Nalgene Beakers. Conductivity and pH were logged every five seconds by an Orion 4-Star pH/Conductivity probe (*Thermo Electron*, Waltham, MA) connected to a laptop computer. Magnesium chloride was selected as a magnesium source due to its high solubility. Magnesium chloride ($MgCl_2$) was added continuously to the sample by a Masterflex peristaltic pump (*Cole-Parmer*, Vernon Hills, IL). Figure 2.1 is a picture of the experimental setup.

Magnesium Chloride Injection in Distilled Water

To ensure that the conductivity meter was responding as theoretically predicted, the conductivity change in distilled water due to $MgCl_2$ amendment was tested. In this experiment, 0.05 mol $MgCl_2$ was continuously injected at a flow rate of 13 mL/min into 1.5 L of distilled water at 24^{o}C for seven minutes; conductivity and pH were monitored continuously for the duration of the experiment.

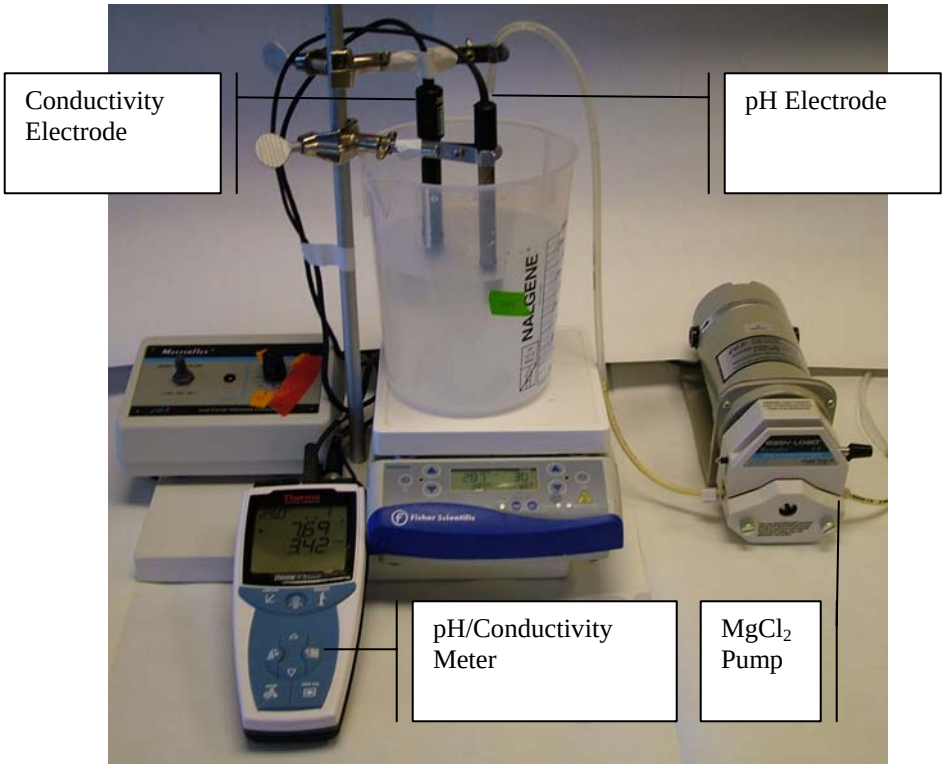

Figure 2.1. Experimental Setup

Magnesium Chloride Injection in PO_4^{3-}:NH_4^+ Solution

Three pure 1.5 L samples of ammonia phosphate were made to simulate the basic struvite reaction. Prior to magnesium injection, the pH of the solution was raised to 8.5 with sodium hydroxide. The solution was continuously stirred and allowed a five-minute reaction time between doses at 24^{o}C. Conductivity and pH were monitored while magnesium was dosed from 10% to 140% of the phosphate stoichiometric requirement at 400, 600, 800, 1000 mg/L PO_4^{3-}.

Magnesium Chloride Injection in Manure

Swine manure slurry samples were collected during custom field application events in the spring of 2006 from six swine production facilities in Iowa. Samples were stored in 5-gallon sealed plastic buckets at 4^{o}C. Each sample was analyzed at

25 ^{o}C in triplicate for dissolved reactive phosphorus (PO_4^{3-}), ammonia (NH_3), and total solids (TS). Dissolved reactive phosphorus concentration analysis used Standard Method 4500-P E (APHA 1998). Ammonia concentration analysis used Standard Method 4500-NH_3 B & C for (APHA 1998). Total solids concentrations analysis used Standard Method 2540 B (APHA 1998). Table 2.2 provides a description of the facility operation and sampling information including animal type, manure storage system, and the time the sample was collected during pump-out

Table 2.2. Facility Information

Sample	Storage	Pump-out Stage
Finisher 1	Lagoon	Very bottom
Finisher 2	Holding Tank	Prior to agitation
Finisher 3	Lagoon	Middle
Finisher 4	Deep Pit	Top
Farrowing 1	Deep Pit	Middle
Farrowing 2	Deep Pit	End

Table 2.3 identifies the physical and chemical results from analysis. Time to saturation, T_{sat}, identifies the $MgCl_2$ pump time required to achieve a 1:1 stoichiometric ratio based on initial phosphate concentration. T_{sat} was used to maintain a relatively equal magnesium injection rate between manures and varied depending on the manure characteristics; triplicates of a manure sample used a fixed T_{sat}. Note that samples Finisher 3 and Farrowing 2 did not maintain a stable reading for the duration of the test; no further testing was performed on these samples. Conductivity and pH for each manure sample was monitored until 250% of the initial stoichiometric phosphate requirements had been applied (2.5 times T_{sat}).

Table 2.3. Physical and Chemical Description of Manure Samples

Sample	PO_4^{3-} mg/L	TS, %	NH_4^+ mg/L	T_{sat}, min
Finisher 1	130	4.7	1800	4.5
Finisher 2	620	4.6	4600	5.0
Finisher 3	500	1.4	2300	4.1
Finisher 4	950	6.4	4400	*no stable conductivity reading
Farrowing 1	390	2.4	2900	4.7
Farrowing 2	390	8.0	NA	*no stable conductivity reading

To identify the point when struvite precipitation was maximized, a second test on sample Finisher 4 was performed. This experiment monitored the conductivity and pH as described above. However, the amount of magnesium injection time was increased to approximately 700% of the initial stoichiometric phosphate requirements (7 times T_{sat}). Triplicate 30 ml samples were extracted prior to pH adjustment, after pH adjustment, every two minutes for the duration magnesium injection, and after magnesium injection was complete for DRP analysis.

Results

Magnesium Chloride Injection in Distilled Water

Experimental measurements obtained were plotted with theoretical predictions of conductivity at equal concentrations. Figure 2.2 shows the comparison of the experimental and theoretical results. This plot shows that the experimental data is in agreement with the theoretical calculations of conductivity.

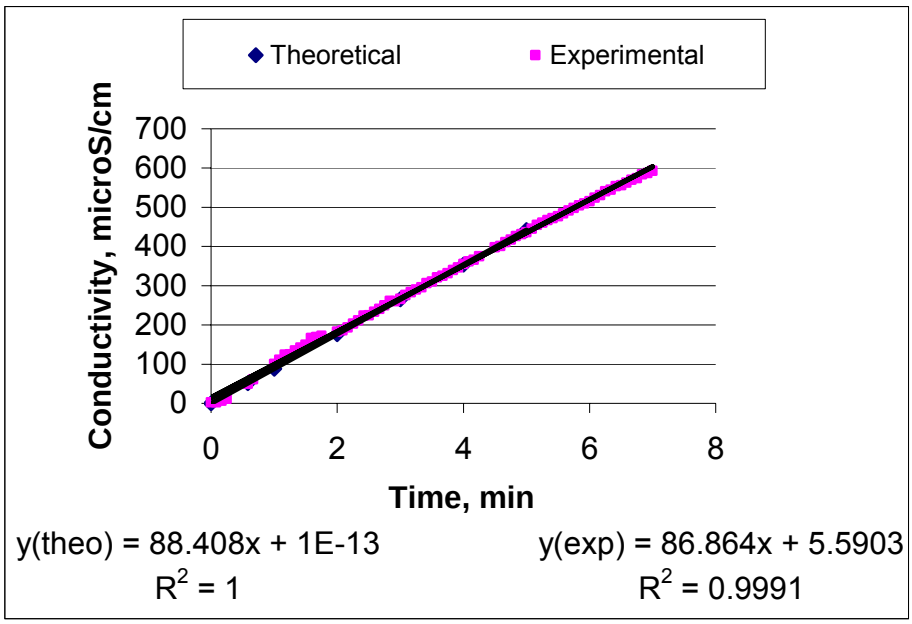

Figure 2.2. Comparison of Theoretical Model and Experimental Data in Distilled Water

Magnesium Chloride Injection in PO_4^{3-}:NH_4^+ Solution

Figure 2.3 plots the experimental and theoretical curves of $MgCl_2$ injection into PO_4^{3-}:NH_4^+ Solution .The theoretical model of conductivity provides an inflection point that corresponds with magnesium saturation and optimized struvite precipitation. As struvite is formed, phosphate, ammonium, and magnesium are removed from solution while chloride is added. The change in specific conductance is positive and linear during this portion of the reaction. When phosphate or ammonia becomes the limiting ion, struvite no longer precipitates; with continued injection of magnesium chloride, both magnesium and chloride ions enter solution while no ionic removal occurs. The change in specific conductance then provides a slope approximately 20 times greater than when struvite was formed. The change in

conductivity slope could be used to identify magnesium saturation and optimized struvite formation.

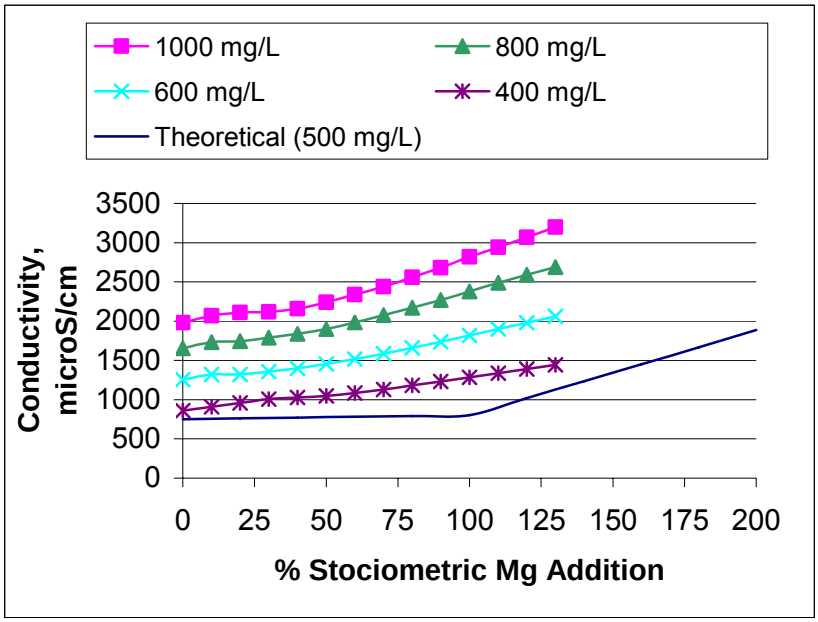

Figure 2.3. Comparison of Theoretical Model and Experimental Data in PO_4^{3-}-NH_4^+ Solution

Magnesium Chloride Injection in Manure Slurries

To determine if this process was applicable over a broad range of operation systems, several manures were collected from other swine farms (as listed in Table 2.2). Triplicate experiments developed conductivity curves for these manures. Figures 2.4 through 2.7 illustrate the conductivity response curves from the four swine facilities, with no inflection point indicating the magnesium demand for struvite precipitation; furthermore each manure provided a negative slope contradictory to theoretical predictions. Based on this information, it would not be possible to determine the magnesium demand by monitoring conductivity.

To identify the exact point of phosphate removal, tests were performed on Finisher 3 over an increased magnesium injection amount. Finisher 3 was selected because it provided a conductivity response curve with the greatest stability. Excess magnesium was added to ensure that maximum phosphate removal occurred. Samples were recovered throughout the experiment for DRP analysis. Figure 2.8 provides the extended conductivity response curve and the corresponding DRP removal values.

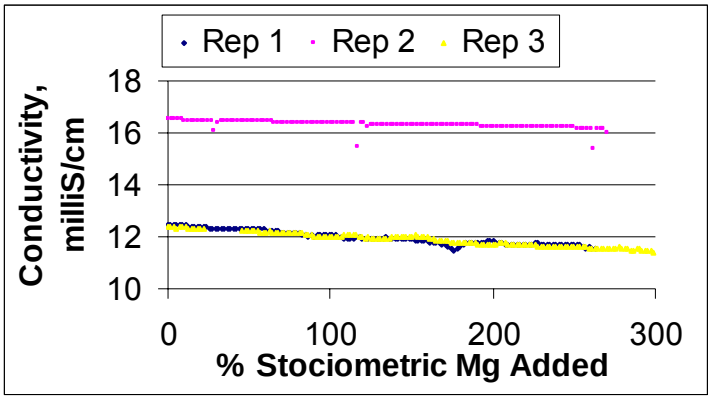

Figure 2.4. Finisher 1: Conductivity Responses to Magnesium Injection

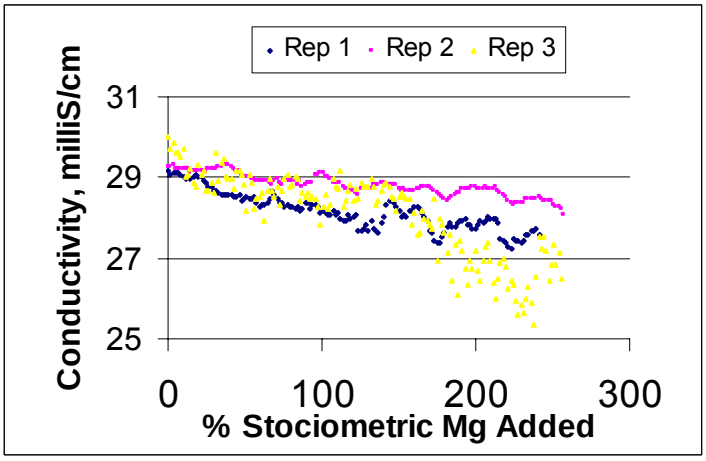

Figure 2.5. Finisher 2: Conductivity response to magnesium injection

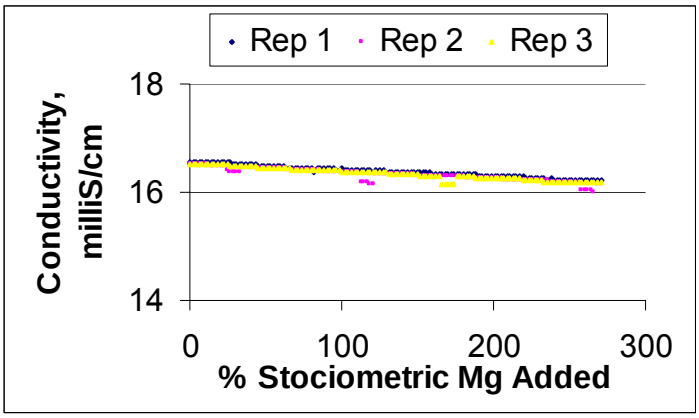

Figure 2.6. Finisher 3: Conductivity response to magnesium injection

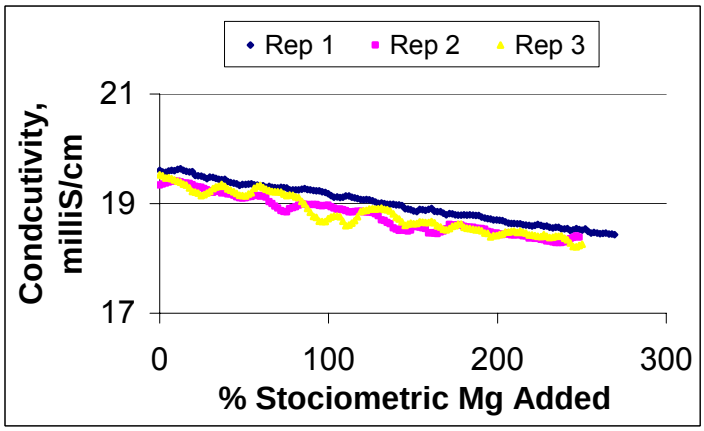

Figure 2.7. Farrowing 1: Conductivity response to magnesium injection

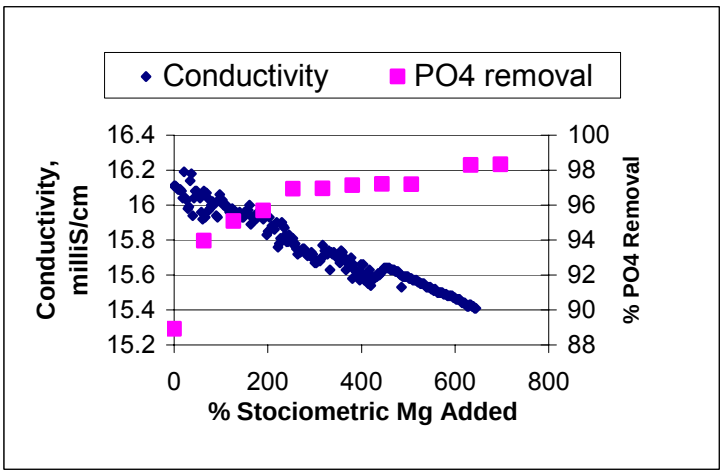

Figure 2.8. Extended Conductivity Response and Phosphate Removal to Magnesium Injection

The phosphate analysis indicated that approximately 88% of the available dissolved reactive phosphorus (DRP) was removed during pH adjustment. The initial pH of 6.85 was adjusted to 8.48 with sodium hydroxide prior to magnesium amendment. This significant reduction of phosphate can most likely be attributed to precipitation of struvite with magnesium initially present in the manure sample and complexing of phosphate with other metal ions such as calcium. The extended magnesium injection failed to produce an inflection point indicating magnesium saturation and optimized struvite precipitation. The lack of an inflection point indicates that when magnesium chloride is added in excess of phosphate requirements, it continues to complex with ions in the solution, reducing the specific conductance of the solution.

Conclusion

The goal of this project was to develop a system that identified magnesium demand for struvite formation by monitoring conductivity changes during continuous injection of magnesium chloride in several different manure slurries. Theoretical predictions and pure solution tests provided information capable of determining the magnesium demand for struvite precipitations. After testing six different manures in triplicate, the conductivity responses did not follow theoretical predictions and failed to provide any indication of optimum magnesium injection rates for phosphorus removal.

Optimized struvite precipitation in a continuous flow reactor requires the ability to define the proper magnesium demand. Current methods of determining the

magnesium injection rates rely heavily upon time-consuming laboratory work, but do not account for variations in manures that occur throughout the treatment period. Magnesium is often applied at molar ratios higher than calculated stoichiometric requirements to achieve maximum phosphate removal (Burns et al. 2003, Bowers and Westerman 2005). These defined magnesium amendment ratios have been developed for specific manures and may not be accurate assumptions for all manure systems.

The conductivity response curves generated from the manure samples have a generally stable and negative slope and do not identify a magnesium saturation point. The constant trend of the conductivity response curve as magnesium is continuously applied after maximum struvite precipitation has occurred, suggests that magnesium continues to complex with organics and other free ions in solution. A magnesium ISE is not a suitable tool to determine the magnesium demand for struvite formation as it may providing an overestimation of magnesium demand.

Based on the findings and experience, the most feasible way of determining a real-time magnesium demand for struvite precipitation would incorporate a phosphate ISE. During magnesium injection, a phosphate ISE would allow the user to directly monitor the level of dissolved reactive phosphorus in solution and thus indirectly monitor struvite formation. The indication of optimum struvite formation would be identified when the desired phosphate concentration is achieved, while avoiding errors due to magnesium complexing. Current methods of in-situ phosphate monitoring incorporate colorimetric methods that are prone to fouling in manure systems. The development of a phosphate ISE that is capable of withstanding the

harsh environment of manure slurries would allow a producer to indirectly monitor the magnesium demand for struvite precipitation in real-time.

Acknowledgements

This project is funded by a grant from the USDA NRI contract number 20033550415627.

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CHAPTER 3

DEVELOPMENT OF A BENCH-SCALE AIR SPARGED CONTINUOUS FLOW REACTOR FOR STRUVITE PRECIPITATION FROM TWO DIFFERENT LIQUID SWINE MANURE STORAGE SYSTEMS

Submitted for publication in *Biosystems Engineering*

Timothy A. Shepherd, Robert T. Burns, Lara B. Moody, D. Raj Raman, Keneth J. Stalder

Abstract

Forced precipitation of struvite ($MgNH_4PO_4*6H_2O$) can reduce dissolved reactive phosphorus (DRP) in swine manure slurries. Optimization of this process requires that the swine manure slurry pH be increased, that magnesium be added, and that sufficient reaction time be allowed for struvite precipitation. To gather data that could be used for a full-scale continuous-flow struvite precipitation reactor, a bench-scale (14-L) continuous flow reactor was designed, constructed, and tested. The bench-scale reactor used air sparging for both pH adjustment and mixing, used a peristaltic pump to continuously inject magnesium chloride ($MgCl_2 \cdot 6H_2O$), and was operated at a 10-minute hydraulic retention time. The bench-scale system provided a 95% reduction of DRP in swine manure slurry collected from a concrete storage tank with a permeable cover, and a 78% reduction of DRP in swine manure slurry collected from a shallow under floor pit collection system. The implication of this work for full-scale systems is discussed.

Keywords: Manure, Phosphorus, Struvite, Swine

Introduction

Growing water quality and land management concerns have resulted in new requirements for the land application of manure slurries. These requirements frequently appear as regulations to limit the application of manure slurries based on crop macronutrient needs, such as nitrogen or phosphorus (Shober and Simms, 2003). In many cases, the maximum allowable slurry application rate is limited by the phosphorus content of the slurry, meaning that phosphorus removal systems could allow higher application rates of manure slurry. One such approach is the forced precipitation of the crystalline precipitate struvite (magnesium ammonia phosphate hexahydrate, $MgNH_4PO_4*6H_2O$).

Forced precipitation of struvite can significantly reduce the amount of soluble phosphorus (reported as dissolved reactive phosphorus, or DRP, in this paper) in manure slurries, while simultaneously concentrating phosphorus for recovery and future use (Bowers and Westerman, 2005a; Burns et al., 2001; Munch and Barr, 2001; Ohlinger et al., 2000). In laboratory and field tests, forced struvite precipitation has been shown to remove 90% or more of the DRP from swine manure slurry (Burns et al., 2001). Recovered struvite can be used as a slow-release commercial or agricultural fertilizer, offering potential as an added value byproduct (de-Bashan and Bashan, 2004). Furthermore, controlling the amount of phosphorus removed during treatment will allow adjustment of nitrogen to phosphorus ratios, providing the potential to balance N and P to match crop requirements.

In a pure solution, a 1:1:1 (Mg^{2+}: NH_4^+:PO_4^{3-}) molar ratio will form struvite (Burns et al., 2001). The rate of struvite formation depends upon the conditional

solubility product (K_{sp}) of struvite which is directly proportional to the product of Mg^{2+}, NH_4^+, and PO_4^{3-} ions in solution. The precipitation potential of struvite is highly dependant on K_{sp} and solution pH; as pH increases, the dissolution/precipitation equilibrium curve for struvite decreases allowing a greater degree of struvite precipitation to occur (Ohlinger et al., 2000). Struvite formation increases with pH until it reaches its maximum precipitation point near a pH level of 9.0 (Buchanan et al., 1992). However, increasing pH also increases volatilization of ammonia; therefore, excessive pH increases should be avoided.

In typical manure slurries, Mg^{2+} is the limiting ion for optimized struvite formation; therefore, magnesium addition is required to maximize DRP removal. Furthermore, in heterogeneous organic solutions such as manure slurries, magnesium complexes with other ions in solution, thus magnesium additions greater than stoichiometric requirements may be needed to overcome competing reaction (Burns et al., 2003; Celen et al., 2007).

Currently, there are several treatment systems that apply struvite precipitation techniques for phosphorus removal in municipal and industrial wastewaters (Munch and Barr, 2001; Ohlinger et al., 2000). Full-scale struvite reactors have been incorporated into municipal and industrial wastewater treatment systems in Japan and Europe but their implementation is not common practice in livestock production facilities (Burns et al., 2003).

Bowers and Westerman (2005a) developed a cone-shaped fluidized bed reactor for treatment of swine wastewater. Their system utilized a fluidized bed containing struvite to promote the growth of struvite crystals within the reactor.

Modeling and testing indicated that the conical reactor created plug-flow conditions for the liquid and provided a completely mixed fluidized bed. Field tests demonstrated DRP removal rates ranging from 13% to 80%, with low performance associated with low particle size. This occurs because small particles have low settling velocities, and are more likely to be washed out of the reactor, as observed by Munch and Barr (2001). To overcome this, Bowers and Westerman (2005b) reduced the flow rate through the reactor to maintain struvite settling in order to ensure that struvite and bed washout did not occur.

With the inconsistent nature of manure slurries, a rapid increase in TS of the influent slurry has the potential to create a similar washout effect in fluidized bed reactors and thus provide lower than expected phosphorus removal rates. Additionally, organic matter and other suspended particles could interfere with the struvite bed particles and reduce the precipitation potential of struvite on the bed particles by promoting the spontaneous nucleation of fine struvite particles. Fine struvite particles have lower settling velocities than larger particles and can become entrained in the effluent. Finally, fluidized bed reactors are complex in design, fabrication, and operation. For these reasons, we examined the potential of an alternate reactor configuration – that of a continuously stirred tank reactor followed by a downstream separation system to achieve struvite-based phosphorus removal from swine manure slurries.

Manure slurry treatment systems that can perform at relatively high flow rates under variable environmental conditions are desirable for implementation within existing swine production systems. When treating swine manure slurry, the most

convenient point for DRP removal occurs during land application of the slurry. Manure slurry characteristics (solids content, nutrient concentrations, pH) can change during field application events. Changes during a field application event require a treatment system that is robust, tolerant of variable influents, and flexible. Furthermore, manure slurry application systems operate at flow rates ranging from 1,900 – 5,700 L/min (500-1,500 gpm). This high volume application rate requires a treatment system with comparable flow rates, necessitating short retention times to avoid excessively large reactors. A flexible system requires an easily modifiable design that can accommodate differences between manure slurry management strategies and manure slurry characteristics from different manure slurry storage systems involving a variety of livestock species.

Continuous flow stirred tank reactors (CSTRs) inherently buffer shock loading (Benfield and Randall, 1987); making them less susceptible to the anticipated variability in manure slurries. Continuous flow stirred tank reactors are relatively simple in design, and their sizing is well defined (AWWA, 1999). The simple design parameters also provide operational and maintenance benefits associated with startup and process changes that may not be available with fluidized bed reactors.

The objective of this study was to develop and test a short-retention-time bench-scale CSTR, capable of effectively and reliably reducing DRP from swine manure slurries.

Materials and Methods

Bench-scale Design

A 19-L (5-gal) plastic bucket was chosen as the vessel for the 14-L (working volume) bench-scale air sparged continuous flow tank reactor (ASTR, Figures 3.1 and 3.2). A fine bubble EDI PermaCap 5 diffuser (*Environmental Dynamics Inc*., Columbia, MO) was mounted at the bottom of the reactor to provide diffused aeration for mixing and pH adjustment. Manure slurry was pumped into the reactor at 1.4 L/min by a utility pump (Model 75982, *Wayne Water Systems*, Harrison, OH), providing a 10-minute HRT. The influent passed through 0.6 cm copper tubing discharging directly above the air diffuser plate to provide rapid mixing of the influent. Magnesium chloride was injected with a Masterflex peristaltic pump (Model 7518-10, *Cole Palmer*, Vernon Hills, IL) through 0.3 cm copper tubing discharging directly above the diffuser plate to provide incorporation with the manure slurry. For simplicity during initial testing of the system, magnesium was applied in excess to insure maximum phosphate removal. The magnesium injection rate was determined from initial DRP analysis and then adjusted to achieve the Mg^{2+}:PO_4^{3-} ratio of 1.6:1 (per Burns et. al, 2003). The effluent was collected near the center of the ASTR to discourage short-circuiting within the reactor.

Three commercial and one lab-fabricated air diffusion plates were tested to determine the gas transfer characteristics and mixing capabilities. Three PermaCap 5 (*Environmental Dynamics Inc.*, Columbia, MO) diffuser types provided fine, medium, or coarse air bubble sizes at similar flow rates. Diffusers were tested to identify the pH adjustment capabilities for air flow rates between 15-35 L/min.

The ASTR system alone does not provide a mechanism for the recovery of the precipitated phosphorus. Struvite has a specific gravity of 1.7, while liquid swine manure has a specific gravity near 1.0; this difference should permit gravity or centrifugal separation for the ultimate removal and recovery of precipitated phosphorus from the manure slurry. For the bench-scale study, we employed a 36.6-L up-flow clarifier (UFC), placed downstream of the ASTR (Figure 3.3). Up-flow clarifiers are commonly used in municipal wastewater treatment systems to separate solids from liquids in continuous flow systems (AWWA, 1999). The UFC employed here had a diameter of 0.36 m, a total volume of 36.6 L, received slurry at 0.7 L/min, and therefore had a 52 min detention time. The UFC weir was designed to provide a surface overflow rate of 32 $m^3day^{-1}m^{-2}$ (Metcalf and Eddy, 1991).

Manure Slurry Sources

Manure slurries were collected from two production facilities utilizing different manure slurry storage systems. The initial manure slurry was collected from a commercial finishing facility near Ames, Iowa. This system employed a 1-year capacity storage tank covered with light expanded clay aggregate (LECA). At the time of sampling, the storage tank was at approximately two-thirds of the total capacity. The second manure slurry was collected from the Iowa State University Swine Teaching Facility (Ames, Iowa), which is a swine finish facility. This system employed an under floor shallow-pit in the finishing barn which was pumped to a secondary storage tank weekly; manure slurry was collected from the shallow-pit.

Sample Analysis

Chemical analysis methods were as follows: dissolved reactive phosphorus - Standard Method 4500-P E (APHA, 1998); total phosphorus - Standard Method 965-17 (AOAC, 2002); total Kjeldahl nitrogen (TKN) - Standard Method 2001-11 (AOAC, 2000); ammonium (NH_4^+) - Standard Method 4500-NH_4 B & C for (APHA, 1998); total solids - Standard Method 2540 B (APHA, 1998). Solution pH was determined with a pH electrode (Orion 4-Star pH/Conductivity probe, *Thermo Fisher Scientific*, Waltham, MA) calibrated with 7.0 and 10.0 standard pH solution prior to each determination.

Bench-scale Operation

Treatment of swine manure slurry for DRP reduction in the bench-scale ASTR proceeded in two phases: a pre-aeration batch phase followed by a continuous-flow DRP-precipitation phase (Figure 2.4). Pre-aeration consisted of applying diffused air at a flow rate of 20 L/min for 30 minutes to provide the initial 0.5 unit pH adjustment to 14 L of untreated manure slurry. After the initial pH increase was achieved in batch mode, untreated manure slurry was injected into the ASTR at 1.4 L/min to achieve continuous flow operation. During this time, magnesium chloride was continuously injected at a rate determined from laboratory analysis to achieve a 1.6:1 Mg^{2+}:PO_4^{3-} molar ratio, air sparging proceeded at 20 L/min, and treated manure slurry was continuously extracted at 1.4 L/min.

To test the ASTR-UFC system, the UFC was pre-loaded with effluent from the ASTR, and then the ASTR and UFC were both operated in continuous flow modes

for 60 minutes. For the duration of UFC pre-loading and continuous flow operation, influent and effluent samples were collected from the ASTR and UFC.

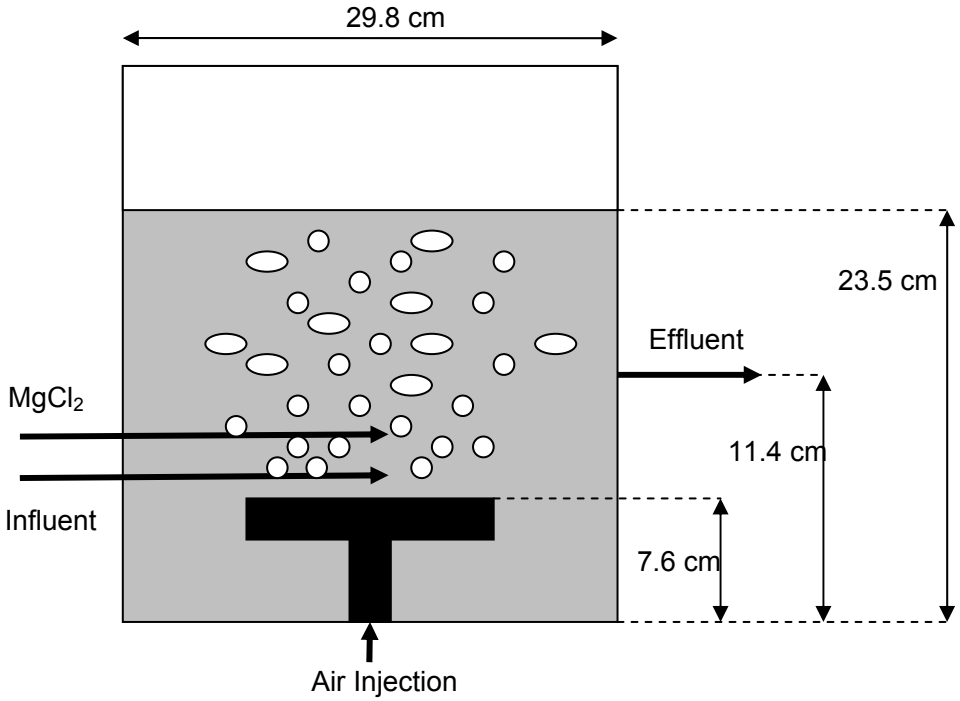

Figure 3.1. Plan drawing of 14-L air sparged continuous flow tank reactor (ASTR)

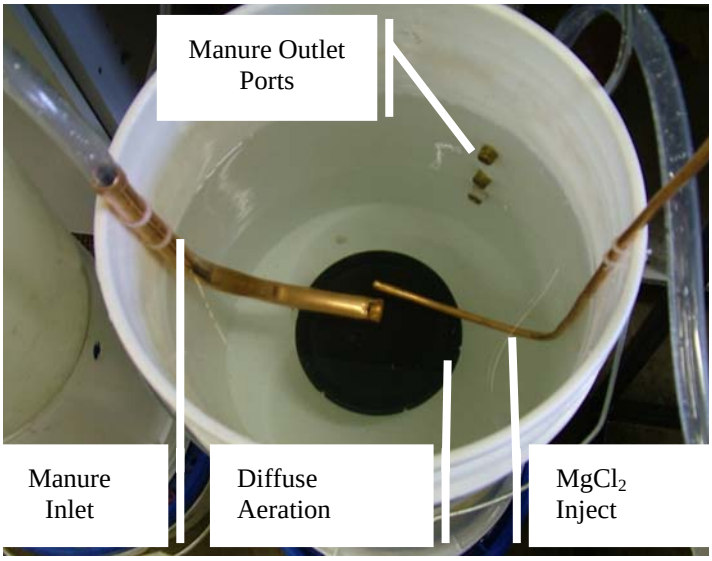

Figure 3.2. Photograph of 14-L air sparged continuous flow tank reactor (ASTR)

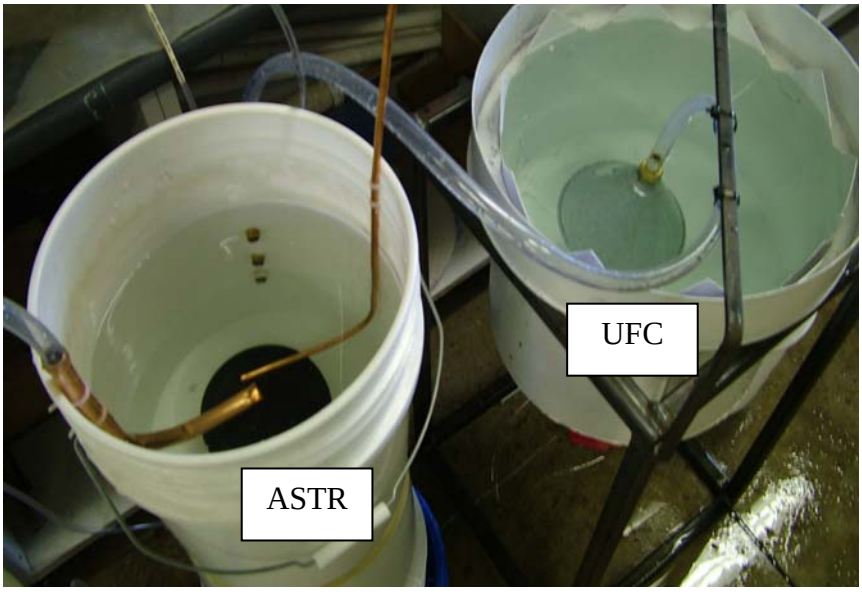

Figure 3.3. Photograph of 14-L air sparged tank reactor (ASTR) in series with an up-flow clarifier (UFC).

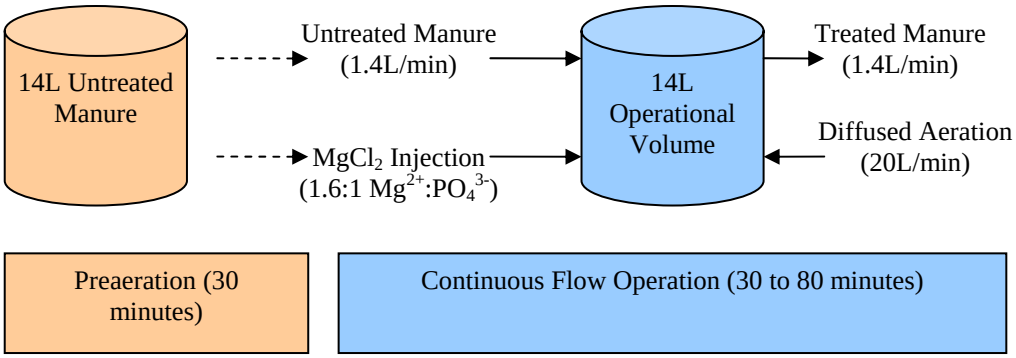

Figure 3.4. Operational flow chart of the air sparged tank reactor (ASTR) for the precipitation of phosphorus from liquid swine manure.

Experiments and Results

ASTR Performance

Table 3.1 provides the nutrient analysis of the two, untreated manure slurries utilized in the treatments. Initial testing of the aeration system indicated that the commercial diffusers outperformed the lab-fabricated diffuser, and the fine bubble diffuser provided the best gas transfer. The fine bubble diffuser appeared to provide vigorous mixing in the ASTR.

Manure slurry from the shallow-pit system was used for the duplicate, 60-minute treatments that were performed to assess the DRP reduction of the ASTR. Pre-aeration provided a pH increase from 7.84 to 8.31 in the first treatment and 7.76 to 8.24 in the second treatment. Figure 3.5 provides the analysis of DRP for the duration of the 60-minute treatments. The system achieved an average DRP reduction of 78% over 30 minutes of continuous flow operation. Additionally, during the second run, a sample collected after pre-aeration and prior to magnesium addition exhibited a 50% reduction in DRP, indicating some of the reduction was due to the pH increase alone.

ASTR-UFC Performance

Manure slurry from the covered storage system was used for the 110-minute treatment with the ASTR-UFC system for the reduction of DRP during pre-aeration and continuous flow operation, and TP removal performance of the UFC. Pre-aeration provided a pH increase from 7.64 to 8.15. Figure 3.6 provides the analysis of DRP and TP for the duration of the 110-minute treatment. While treating manure slurry collected from the covered storage system, the ASTR achieved an average

DRP reduction of 95% for the 80 minutes of continuous flow operation. The ASTR DRP removal did not change from 30 to 80 minutes, suggesting that steady-state was achieved. The sample collected after pre-aeration and prior to magnesium injection exhibited a 68% reduction in DRP. Total phosphorus comparisons of the ASTR influent and UFC effluent indicated that there was no significant removal of total phosphorus through the system.

Table 3.1. Characteristics of the two untreated manure sources: Dissolved reactive phosphorus (DRP), Total Phosphorus (TP), Total Kjeldahl Nitrogen (TKN), Ammonium (NH_4), Total Solids (TS).

Source	DRP[c], mg/L as PO_4^{3-}	TP[d], mg/L as PO_4^{3-}	TKN[e], mg N/L	NH_4[f], mg NH_4-N/L	TS[g], %
Ames Producer Covered Storage[h]	770 ± 14	990 ± 80	--	--	4.6 ± 0.1
ISU Teaching Shallow Pit[i]	264 ± 26	2190 ± 35	2950 ± 60	1460	3.9 ± 0.1

[c] Dissolved Reactive Phosphorus. Standard Method 4500-P E (APHA, 1998)
[d] Total Phosphorus. Standard Method 965-17 (AOAC, 2002)
[e] Total Kjeldahl Nitrogen. Standard Method 2001-11 (AOAC, 2000)
[f] Ammonium Nitrogen. Standard Method 4500-NH_3 B & C for (APHA ,1998)
[g] Percent Total Solids. Standard Method 2540 B (APHA, 1998)
[h] Manure collected from a commercial finishing facility near Ames, Iowa. This system employed a 1-year capacity storage tank covered with light expanded clay aggregate (LECA)
[i] Manure collected at the Iowa State University Swine Teaching Facility (Ames, Iowa) from an under floor shallow-pit in the finishing barn.

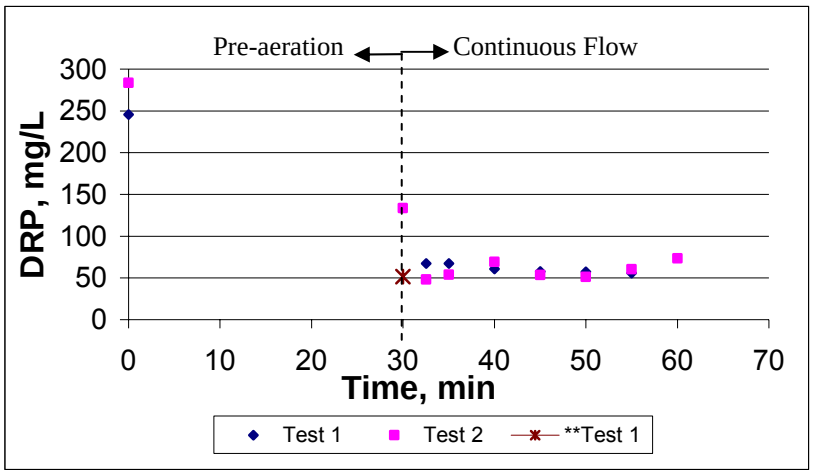

Figure 3.5. Reduction of Dissolved Reactive Phosphorus (DRP) during pre-aeration and continuous flow operation of the air sparged tank reactor (ASTR) with manure collected from the shallow pit manure system.**

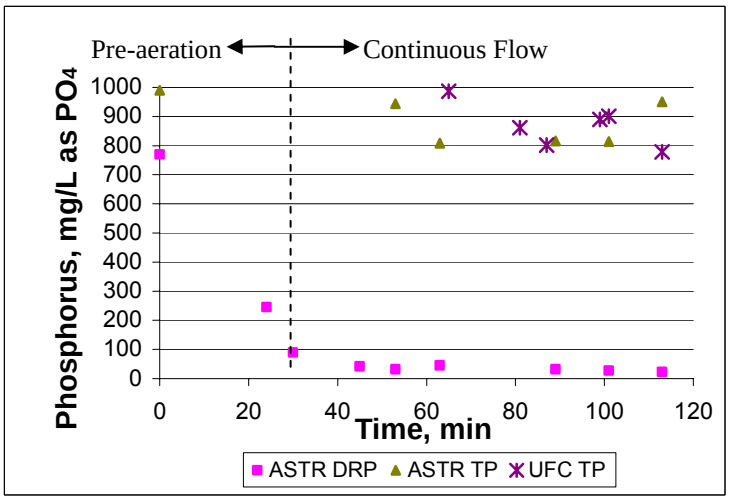

Figure 3.6. Reduction of Dissolved Reactive Phosphorus (DRP) and Total Phosphorus (TP) during pre-aeration and continuous flow operation of the air sparged tank reactor-up-flow clarifier (ASTR-UFC) with manure collected from the covered storage tank.

** Sample collected shortly after magnesium injection was initiated

Discussion

The ASTR system provided an average DRP reduction of 95% with manure slurry from the covered storage system and 78% with manure slurry from the shallow-pit storage system. The difference in DRP reduction rates is most likely due to the amount of DRP available for struvite precipitation and its relation to the conditional solubility product of struvite. Specifically, manure slurry from the covered storage system had significantly higher initial DRP (770 mg/L) than did manure slurry from the shallow-pit (264 mg/L). The ASTR treatment provided an average DRP effluent concentration of 41 mg/L using manure slurry from the covered storage system and 64 mg/L using manure slurry from the under floor shallow-pit system. Ohlinger *et al.* (2000) indicated that a decrease of any contributing species decreases the conditional solubility product of the system and reduces the precipitation potential of struvite. If DRP is reduced significantly, the conditional solubility product and struvite precipitation potential will also decrease. This indicates that the reduction of DRP within the ASTR can limit the precipitation potential of struvite and thus limit the overall phosphorus removal capabilities.

The initial step in struvite precipitation is pH adjustment. Ohlinger *et al.* (2000) found that the solubility of struvite was highly pH dependant; as pH increases within a system, the precipitation potential of struvite is increased. Burns et al. (2003), typically increased swine manure slurry pH up to one unit during their study; improving phosphorus removal via struvite precipitation. As operated here, the ASTR provided an adjustment of 0.5 units during continuous flow operation; further pH adjustment may achieve higher phosphorus removal rates. Consideration of

chemical and energy costs should be accounted for when determining the pH adjustment level to provide the most economically feasible treatment system while maintaining appropriate phosphorus removal rates.

Pre-aeration provided a significant reduction of DRP without magnesium addition, (50% and 68% in samples tested). Two mechanisms can be identified that account for this reduction: magnesium was present prior to treatment allowing for struvite formation after pH adjustment, or phosphate was precipitated as another species such as calcium phosphate, brushite, or monetite. Magnesium is common in most ground water sources and is associated with water hardness; furthermore, some magnesium salts, albeit small amounts, are commonly used in swine rations. The quantity of available magnesium in the raw manure slurry was not determined and X-ray diffraction was not used to identify precipitated species in this study. Implementation at full scale should include a determination of initial magnesium concentrations in raw manure slurries available for struvite formation. Magnesium available for struvite precipitation prior to pH adjustment could reduce or eliminate the need for magnesium amendment.

Several chemicals can be utilized for phosphate removal in wastewaters. The most common include lime, ferric and aluminum salts, magnesium hydroxide ($Mg(OH)_2$), magnesium oxide (MgO), and magnesium chloride ($MgCl_2$). Adding lime or metal salts does not precipitate struvite; however they do complex with phosphate to form precipitants under the same principles. Magnesium hydroxide, MgO, $MgCl_2$, are all viable magnesium sources to force struvite formation. Magnesium hydroxide and MgO have low solubility characteristics and would require dissolving in water

(slacking) prior to amendment similar to lime softening systems for effective implementation. Without slacking prior to amendment, the reaction times required for struvite precipitation would be significantly increased due to the low solubility of $Mg(OH)_2$ and MgO, 0.0012 g/100g H_20 and 0.00062 g/ 100g H_20, respectively. Slaking systems are difficult to operate with consistency and can create issues with amendment accuracy. Miles and Ellis (2001) utilized $Mg(OH)_2$ and MgO to force precipitation; however, the low solubility and precipitation potential of $Mg(OH)_2$ prior to amendment reduced amendment accuracy. Magnesium hydroxide and MgO increase the pH of the solution, reducing the pH adjustment requirement for optimized struvite precipitation. Magnesium chloride has a high solubility, 54.2 g/100g H_20, making it easier to handle and reduces the required reaction time in comparison to $Mg(OH)_2$ and MgO (Burns et al., 2001). However, $MgCl_2$ is acidic and may reduce solution pH, requiring greater pH adjustment to optimize struvite precipitation. For agricultural applications, the use of $MgCl_2$ can reduce equipment cost and labor while increasing the accuracy of dosing when compared to the use of less soluble magnesium compounds.

The incorporation of the UFC did not provide a significant reduction of TP. These results indicate that the settling characteristics of the manure slurry and particle characteristics of the precipitated phosphorus did not allow for continuous removal of the precipitant with the ASTR-UFC system. Precipitant removal strategies that could be incorporated with the ASTR system include operating the ASTR as a sequencing batch reactor to allow a quiescent period for settling, or providing forced gravitational separation in place of the UFC. Further experimentation with other

methods of struvite recovery, such as centrifuging the ASTR treated manure slurry will be conducted in the future to identify the capability for solids separation and TP reduction following treatment.

A typical corn crop in Iowa requires 0.50 – 0.54 kg N/25 kg of grain produced (1.1 to1.2 lb N/bu) and 0.17 kg P_2O_5/25 kg of grain produced (0.375 lb P_2O_5/bu) (Iowa State University, University Extension, 2003). This suggests that manure slurries should have a N:P_2O_5 ratio of 3:1 for land application at a rate which balances both N and P for a typical Iowa corn crop.

The manure from the commercial swine production facility utilizing covered storage contained 78% of the TP in DRP form. This high DRP:TP ratio allows for a significant removal of TP if the precipitated phosphorus can be recovered. Based on the ASTR DRP reduction performance, 73% of the TP could theoretically be recovered as a precipitate, reducing the initial TP concentration of the manure slurry collected from the covered storage from 740 mg/L P_2O_5 to 200 mg/L P_2O_5 (6.2 lb P_2O_5/1000-gallon to 1.7 lb P_2O_5/1000-gallon).

The manure tested which was stored in a shallow-pit system contained 12% of the TP in DRP form, this low DRP:TP ratio reduces the overall amount of phosphorus that can be removed via struvite precipitation and separation. Based on the ASTR DRP reduction performance, 9% of the TP could theoretically be recovered as precipitate, reducing the initial TP concentration of the manure collected from the shallow-pit storage from 1640 mg/L P_2O_5 to 1440 mg/L P_2O_5 (13.7 lb P_2O_5/1000-gallon to 12.0 lb P_2O_5/1000-gallon).

Untreated manure slurry from the shallow pit storage had a $N:P_2O_5$ ratio of 1.8:1; if applied at nitrogen levels for a typical corn crop in Iowa, phosphorus would be applied in excess. Treatment with the ASTR has the potential to adjust the $N:P_2O_5$ ratio to 2.0:1. To achieve the desired (balanced) $N:P_2O_5$ ratio of 3:1, manure slurry from in this specific system would require at least 60% of the TP to be in the form of DRP for the precipitation and recovery of struvite.

Bowers and Westerman (2005a, b) used struvite precipitation to treat raw swine manure slurry with approximately 50% of the TP available as DRP; they were capable of providing TP removal rates ranging from 49% to 56% with this high DRP:TP ratio. Manure slurries with high DRP:TP ratios can provide a higher phosphorus removal potential, allowing treatment systems to adjust the nutrient removal ratios to provide a N and P balanced manure slurry.

Two reasons for the variation between the DRP:TP ratio from the manure slurries sampled include different feed rations used to feed the pigs grown at the two facilities and manure slurry storage type. Manure slurry from the commercial production facility was collected from a covered storage tank; manure slurry from the Iowa State University Swine Teaching farm was collected directly from the shallow pit below the barn, before the long term storage system. Long term manure slurry storage systems, such as covered storage tanks, would be expected to provide a greater degree of anaerobic digestion than the short term storage of manure slurry found in shallow pit barns. During the anaerobic process, a portion of nutrients such as nitrogen and phosphorus are converted from the organic and relatively non-reactive form, to a more soluble and reactive form. Beal *et al.* (1999) determined that

anaerobic treatment of swine manure slurry increased the concentration of DRP and subsequently enhanced phosphorus removal capabilities via struvite precipitation. Results of the bench-scale test will be used to design a palletized pilot-scale treatment system which will be tested at several Iowa pork operations that utilize various manure slurry management strategies.

Conclusion

A continuous flow bench-scale (14-L) air sparged tank reactor (ASTR) was developed and tested for reducing dissolved reactive phosphorus (DRP) from two different swine manure slurry samples via struvite precipitation. The ASTR used air sparging for both pH adjustment and mixing, used a peristaltic pump to continuously inject magnesium chloride ($MgCl_2 \cdot 6H_2O$), and was operated at a 10-minute hydraulic retention time. Two manure slurry samples that differed in their storage systems [covered storage tank (760 mg/L DRP) and shallow-pit (264 mg/L DRP)] were treated with the ASTR system. The bench-scale system provided a 95% reduction of DRP in swine manure slurry collected from a concrete storage tank with a permeable cover, and a 78% reduction of DRP in swine manure slurry collected from a shallow under floor pit collection system. Treatment with the ASTR provided an average DRP effluent concentration of 41 mg/L with the covered storage tank manure slurry and 64 mg/L with the shallow-pit manure slurry. Increasing the pH without magnesium addition provided significant reductions in DRP in the two swine manure slurries tested. ASTR-UFC system performance indicates that the UFC is not capable of settling struvite particles formed in the ASTR. The failure of the UFC to remove struvite particles was most likely due to the small particle size of

precipitants and the settling characteristics of the manure slurry. This research indicates that a simple, robust, and flexible system utilizing air sparging and magnesium amendment can provide significant reductions of DRP from swine manure slurries. Furthermore, by adjusting $MgCl_2$ amendment rates, a predetermined fraction of DRP can be precipitated as struvite for recovery, allowing site-specific treatment capable of producing a manure slurry fertilizer, which is balanced to meet crop requirement in terms of nitrogen and phosphorus nutrients. Further research will investigate other solid separation techniques and their ability to remove struvite and precipitated phosphorus from ASTR treated manure slurries and determine the economic feasibility of removing phosphorus with the ASTR system.

Acknowledgements

This project is funded by a grant from the USDA NRI contract number 20033550415627.

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CHAPTER 4

PERFORMANCE OF A PILOT-SCALE AIR SPARGED CONTINUOUS FLOW REACTOR AND HYDROCYCLONE FOR STRUVITE PRECIPITATION AND REMOVAL FROM LIQUID SWINE MANURE

To be submitted for publication in *Transactions of ASABE*

Timothy A. Shepherd, Robert T. Burns, D. Raj Raman, Lara B. Moody, Kenneth J. Stalder

Abstract

The development of a dedicated struvite reactor capable of operating at full-scale pork production operations is essential for the implementation for phosphorus reduction via struvite precipitation. The objective of this research was to test a pilot-scale air sparged tank reactor (ASTR) and struvite separation system on two manure slurries for struvite-based phosphorus removal and recovery. The pilot-scale ASTR system operated at flow rates of 80 L/min to 115 L/min and was based on the design from Shepherd et al. (2007). The ASTR effluent was processed using a McLanahan Model S1.506 A20 Hydrocyclone Separator (McLanahan Corp., Hollidaysburg PA) for struvite separation and total phosphorus (TP) recovery. The pilot-scale ASTR system provided a 92% reduction of dissolved reactive phosphorus (DRP) in swine manure slurry from a concrete storage tank, and a 91% reduction of DRP in swine manure slurry collected from a deep-pit under floor collection system. The ASTR-hydrocyclone system removed 18% of TP in swine manure from a concrete storage tank and 9% to 14% of TP in swine manure slurry from a deep-pit under floor collection system. Full-scale economics and implementation of struvite-based phosphorus removal is discussed. A case study of a typical Iowa deep-pit

swine production facility (10,000 head/year) indicated that the annual cost of struvite-based phosphorus removal would be approximately $22.20/pig space or $0.0353/L manure slurry treated ($ 0.134/gal). This indicates that struvite-based phosphorus removal using this system in deep-pit swine manure slurries is not currently economically viable.

Introduction

Growing concerns about water quality and land management have resulted in new requirements for the land application of manure, often in the form of legislation; these regulations often limit the application of manure based on crop nutrient needs, such as phosphorus (Shober and Simms, 2003). Phosphorus based manure application rates can require up to eight times the land required for nitrogen based application rates (Burns et al, 1998). In addition to larger land requirements, application of supplemental nitrogen may be needed for optimal crop production. The development of an economical, robust, and flexible continuous flow struvite precipitation reactor, for phosphorus removal could greatly benefit livestock operations.

Shepherd et al. (2007) developed a novel, bench-scale continuous flow air sparged tank reactor (ASTR) for struvite precipitation in swine manure slurries. The bench-scale ASTR system provided dissolved reactive phosphorus (DRP) reductions of 78% and 93%; however, separation of precipitated struvite for total phosphorus (TP) reduction was not achieved with a continuous flow upflow clarifier. Untreated and ASTR treated manure slurries were tested in the lab to identify struvite removal and recovery possibilities. Centrifuge tests applying more than 80

gravities concentrated phosphorus in ASTR treated manures. The bench-scale centrifugue tests indicated that a hydrocyclone, providing 80 gravities or more may provided a continuous flow method to remove and recover precipitated phosphorus from ASTR-treated manure slurries.

The objectives of this research were to test a continuous flow pilot-scale ASTR utilizing a hydrocyclone solid separator for struvite-based phosphorus removal and recovery.

Optimized struvite precipitation in manure slurries generally requires adding magnesium and increasing the slurry pH. For reaction and energy input efficiency, the optimal time for implementing a continuous flow struvite reactor is during the agitation of stored manure prior to and in series with land application events. Agitation provides a homogenous manure mixture and has been shown to increase manure slurry pH (Zhu et al., 2007); reducing chemical and energy costs associated with pH adjustment.

The most common manure slurry storage systems utilized in U.S. pork production include: under floor deep-pit confinements, storage tanks, holding ponds, and anaerobic lagoons. A nutrient removal system could be designed to treat manure over an extended period at low flow rates. However, this strategy necessitates a post-treatment storage system, increasing capital expenditures. Implementing a treatment system in series with field application events requires higher treatment flow rates, but reduces the need for a post-treatment storage system.

Deep-pit manure storage systems require specific management practices to minimize the concentration of hydrogen sulfide gas (H_2S) inside the production facility. To avoid increasing the amount of H_2S released from deep-pit stored manure slurry, agitation is avoided except during field application events. To minimize H_2S risk in deep-pit storage facilities, the most feasible treatment scheme requires a system capable of performing during land application events when agitation is required and planned for.

During land application events, manure slurry is typically applied at rates ranging from 2,300 to 6,800 L/min (500 to 1,500 gal/min). The majority of struvite research has focused on bench and pilot-scale reactors operating at low flow rates. Bowers and Westerman (2005b) tested a field-scale fluidized bed struvite reactor which treated manure slurries at 5.6 and 9.5 L/min (1.5 and 2.5 gal/min). The transition of bench and pilot-scale fluidized bed reactors to full-scale, on-farm systems may be challenging because of their complex design requirements and limited flexibility due to flow limitations associated with bed loss at high fluid velocities. Furthermore, modifications to achieve high flow rates required to make this type of system applicable for use with large modern pork production operations may not be economically feasible.

Materials and Methods

Pilot-scale Design

A continuous flow pilot-scale ASTR was designed and constructed to precipitate phosphorus in liquid swine manure at flow rates up to 200 L/min (53 gal/min) at a 10-minute hydraulic retention time (HRT). The ASTR-hydrocyclone system was

operated at 80 and 115 L/min (21 and 31 gal/min) during continuous flow test runs. Design criteria and operational conditions for the pilot-scale ASTR were based on bench scale research conducted by Shepherd et al. (2007). A McLanahan Model S1.506 A20 Hydrocyclone Separator (*McLanahan Corp.*; Hollidaysburg, PA) was implemented to provide phosphorus precipitant removal from the ASTR effluent. The ASTR-Hydrocyclone system was constructed as a mobile, palletized system, allowing for testing at various swine production sites (Figures 4.1 and 4.2).

A 3,785-Liter (1000-gallon) cone-bottom, polypropylene tank (*Den Hartog Inc*; Hospers, IA) provides the reaction zone for the ASTR. Raw manure was pumped from the manure storage system to the top of the ASTR with a Vogelsang V100-90Q positive displacement pump (*Vogelsang USA*; Ravenna, OH); the ASTR effluent is recovered from the outlet of the cone-bottom tank and pumped to the hydrocyclone with a Vogelsang VX136-140Q positive displacement pump. The liquid discharge from the hydrocyclone overflow is considered to be the final effluent; a portion of the final effluent is recirculated to the ASTR to control operational volume and hydraulic retention time (HRT). Separated solids from the hydrocyclone underflow are collected in a hopper. At an operation volume of 2000 L, a 10-minute HRT is developed with a corresponding system flow rate of 200 L/min. Varying the operational volume and system flow rate, allows for adjustment of HRT for site-specific requirements and optimization.

Mixing and pH adjustment is provided through air sparging. An Ingersoll-Rand Model SS5 air compressor (*Ingersoll-Rand*; Davidson, NC) provides 566 L/min of compressed air to the ASTR at the base of the cone-bottom. A series of nine

Permacap5 Fine Bubble diffusers (*Environmental Dynamics Inc*.; Columbia, MO), were evenly spaced to provide uniform delivery of air for optimal mixing conditions and maximized bubble contact time (Figure 4.3).

Figure 4.1. Palletized pilot-scale air sparged tank reactor with a hydrocyclone separator (ASTR-Hydrocyclone System)

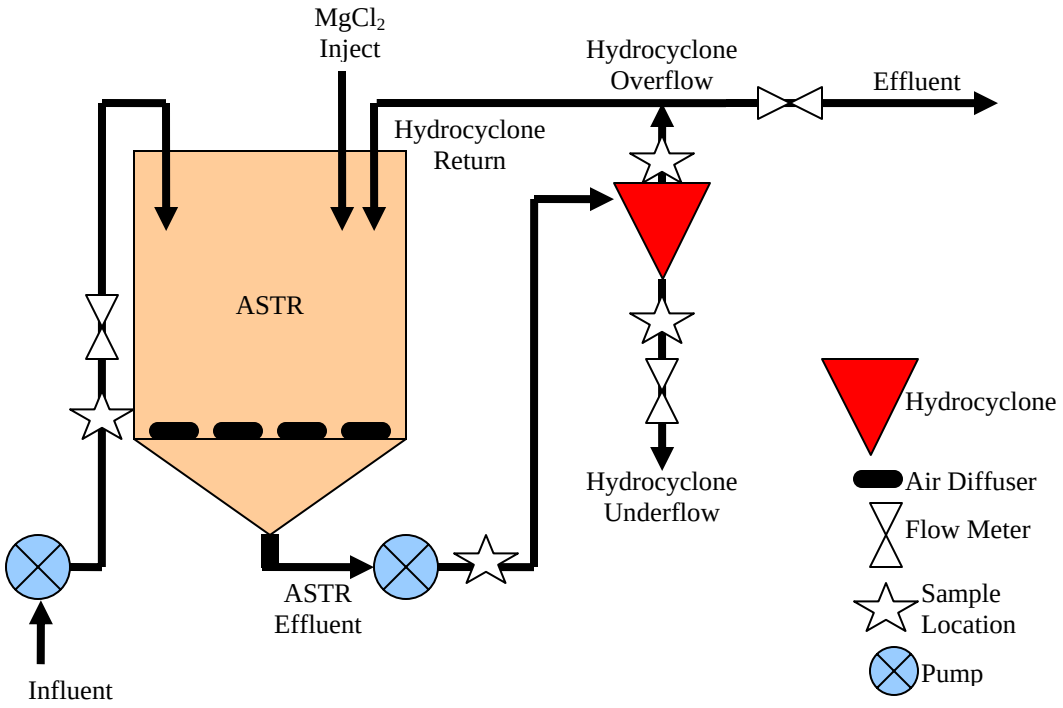

Figure 4.2. Schematic of air sparged tank reactor and hydrocyclone system

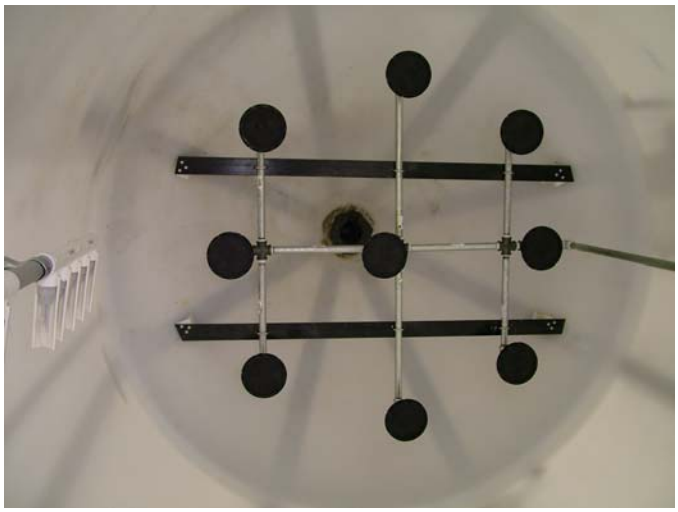

Figure 4.3. Air sparging diffusion platform and liquid level switches

Magnesium chloride ($MgCl_2$) was chosen as the supplemental magnesium source for enhanced struvite precipitation. Magnesium chloride solution (50%) was fed into the ASTR from a 55-gallon drum by a variable speed drum pump (*Standard Pump, Inc.*; Snellville, GA). For simplicity during initial testing of the system, magnesium was applied in excess of stochiometric requirements to insure maximum DRP removal. The magnesium injection rate was determined from initial DRP analysis and adjusted to achieve a Mg^{2+}:PO_4^{3-} ratio of at least 1.6:1 (per Burns et. al, 2003).The magnesium injection site is located at the top of the ASTR near the hydrocyclone return to promote incorporation with the manure slurry.

Two Krohne OPTIFLEX Electromagnetic flow meters (*Krohne, Inc*; Duisburg, Germany), located at the inlet of the ASTR and hydrocyclone overflow discharge, were implemented to monitor and display the flow rates of the influent and effluent. The Influent and hydrocyclone pump were independently controlled with WEG CFW08 variable frequency drives (*WEG Electric Motors LTD.*; Worcestershire, England). The variable frequency drives and flow meters allow for real-time flow rate adjustments to maintain the desired reactor volume and HRT. Liquid level switches were mounted in the reactor to provide indications of volume changes. Air flow regulation was achieved with a gas regulator and monitored with a CDI 5200 digital airflow meter (*CDI Meters*; Belmont, MA). Effluent mass from the hydrocyclone underflow was measured with a Dillon Model GL digital force gauge (*Weigh-Tronix Inc.*; Fairmont, MN). The instrumentation and display system allows for measurements and control of operational conditions.

Pilot-scale Operation

The ASTR-hydrocyclone system was tested in two manure slurries with four 50-minute continuous flow treatments, performed in triplicate: 1) ASTR-Hydrocyclone without aeration or $MgCl_2$ injection, 2) ASTR-Hydrocyclone with aeration, but no $MgCl_2$ injection, and 3) ASTR-Hydrocyclone with aeration and $MgCl_2$ injection. For each treatment, the flow rate to the hydrocyclone was set to achieve a pressure drop of 5 bar across the hydrocyclone; approximately 50% of the hydrocyclone overflow was returned to the ASTR to maintain operational volume and HRT.

Each 50-minute continuous flow operation was divided into five 10-minute time segments for sample collection. Three sub-samples (300mL) were collected for each 10-minute increment at 2, 5, and 8 minutes; sub-samples were pooled for analysis. Influent, ASTR effluent, and hydrocyclone effluent were analyzed as is. Samples of the hydrocyclone underflow were allowed to settle for 48 hours, after which the liquid fraction was decanted with a siphon. The decanted liquid and settled solids were then analyzed separately.

Treatment 1 – ASTR-Hydrocyclone without aeration or $MgCl_2$ injection

The ASTR was primed with 1,900L of manure slurry. Continuous flow operation was then initiated without aeration and $MgCl_2$ injection for 50 minutes.

Treatment 2 – ASTR-Hydrocyclone with aeration but without Mg Cl_2 injection

The ASTR was initially primed with 1,900L of manure slurry. Treatment then proceeded in two phases: a pre-aeration batch phase followed by a continuous-flow DRP-precipitation and separation phase. Pre-aeration consisted of applying diffused air at a flow rate of 566 L/min for 30 minutes to the 2000 L of untreated manure

slurry. After the initial batch phase, continuous flow operation was initiated with air sparging at 566 L/min; $MgCl_2$ was not injected.

Treatment 3 – ASTR-Hydrocyclone with aeration and $MgCl_2$ Injection

The ASTR was initially primed with 1,900L of manure slurry. Treatment proceeded in two phases, with pre-aeration operated as previously described. Following the initial batch phase, continuous flow operation was initiated. During continuous flow operation, $MgCl_2$ was injected at a rate determined from laboratory analysis to achieve a Mg^{2+}:PO_4^{3-} molar ratio of at least 1.6:1; air sparging proceeded at 566 L/min.

Manure Slurry Sources

The ASTR was tested on-site at two swine commercial finishing facilities near Ames, IA. Each site utilized different a manure storage systems, an under-floor deep-pit storage system and a concrete storage tank. Treated manure slurry was returned to the storage system approximately 30 meters from the extraction point. Variations in the hydrocyclone underflow and effluent flow rates required adjustment of the influent flow rate to maintain the operating volume of the ASTR.

The first manure slurry tested was extracted directly from the under-floor deep-pit storage system without agitation. The deep-pit manure was processed with all three treatments of the ASTR-hydrocyclone system. The hydrocyclone flow rate was set at 277 L/min (73 gal/min), the system flow rate was approximately 115 L/min (31 gal/min), and the HRT was approximately 16 minutes.

The second manure slurry tested, from the concrete storage system, was agitated prior to and during testing; only treatment with $MgCl_2$ addition and aeration

was performed. The hydrocyclone flow rate was set at 300 L/min (79 gal/min), the system flow rate was approximately 79 L/min (21 gal/min), and the HRT was approximately 24 minutes.

Sample Analysis

Chemical analysis methods were as follows: dissolved reactive phosphorus - Standard Method 4500-P E (APHA, 1998); total phosphorus - Standard Method 965-17 (AOAC, 2002); total Kjeldahl nitrogen (TKN) - Standard Method 2001-11 (AOAC, 2000); ammonium (NH_4^+) - Standard Method 4500-NH_4 B & C for (APHA, 1998); total solids - Standard Method 2540 B (APHA, 1998); Solution pH was determined with a pH electrode (Orion 4-Star pH/Conductivity probe, *Thermo Fisher Scientific*, Waltham, MA) calibrated with 7.0 and 10.0 standard pH solution prior to each treatment. Statistical analysis of phosphorus concentrations and total mass of phosphorus were accomplished using proc MIXED in SAS software. (*SAS*, 2003).

Results

The air-sparged tank reactor-hydrocyclone system (ASTR-hydrocyclone) was operated under three conditions to identify reductions in dissolved reactive phosphorus (DRP) and total phosphorus (TP) removal capabilities. Table 4.1 provides the nutrient analysis of the untreated manure slurries utilized in the treatments. Two days prior to testing the ASTR-hydrocyclone system, a sample of the deep-pit manure was collected for analysis; the DRP concentration was determined to be 100 mg/L as P. During testing of the ASTR-hydrocyclone system the average DRP concentration of untreated manure was 22 mg/L as P. This difference is most likely due to the collection of an unrepresentative sample prior to

testing. Magnesium amendment rates were determined from the DRP analysis prior to testing (100 mg P /L), resulting in the application of $MgCl_2$ at a ratio of 7.3:1 Mg^{2+}:PO_4^{3-} ratio.

The ASTR portion of the system was designed to provide optimal conditions for DRP precipitation as struvite through pH adjustment, $MgCl_2$ incorporation, hydraulic retention time, and mixing. The ASTR is not designed to remove phosphorus from the slurry. ASTR performance is quantified by DRP reductions through the system. The hydrocyclone was incorporated to provide separation of precipitated phosphorus from the ASTR effluent; hydrocyclone performance is quantified by its ability to concentrate and remove total phosphorus (TP) from ASTR-treated manure slurries.

ASTR Performance

For the deep-pit manure slurry, thirty minutes of pre-aeration provided an average pH increase of 0.24 units from 7.83 to 8.07. Under continuous flow conditions, air sparging without $MgCl_2$ injection maintained a minimum pH increase of 0.11 units, air sparging with $MgCl_2$ injection maintained a minimum pH increase of 0.10 units.

Thirty minutes of pre-aeration provided an average pH increase of 0.25 units from 7.05 to 7.30 with manure slurry from the concrete storage system. The addition of $MgCl_2$ produced an immediately decreased pH to approximately 7.0 prior to continuous flow aeration, suggesting that the manure slurry from the concrete storage had a lower pH buffering capacity than the manure slurry from deep-pit storage. The pH was reduced to approximately 6.95 under continuous flow

operation. Manure slurries with lower buffering capacities may not allow aeration to provide a specific pH adjustment required for optimized struvite precipitation. A caustic amendment system could be implemented for supplementary pH adjustment when aeration is not sufficient.

Table 4.2 provides the DRP concentrations entering and exiting the system, averaged across replications for each treatment. Treatment with air sparging and $MgCl_2$ injection provided 91% reduction of DRP in manure from the deep-pit storage system and 92% reduction of DRP in manure from the concrete storage system during 50 minutes of continuous flow operation. With aeration and $MgCl_2$ addition, the average influent DRP concentration was reduced from 22 mg P /L to 2.0 mg P/L in the deep-pit manure slurry and 130 mg P/L to 11 mg P/L in the concrete storage manure slurry. Treatment without air sparging and without $MgCl_2$ injection provided a 14% reduction in DRP in the deep-pit manure slurry; while treatment with aeration but without $MgCl_2$ did not provide a statistically significant reduction of DRP in the deep-pit manure slurry.

Table 4.1. Characteristics of the untreated manure sources: Dissolved reactive phosphorus (DRP), Total Phosphorus (TP), Total Kjeldahl Nitrogen (TKN), Ammonium (NH_4), Total Solids (TS).

Source	DRP[j], mg/L as P	TP[k], mg/kg as P	TKN[l], mg N/L	NH_4[m], mg NH_4-N/L	TS[n], %
Deep Pit[o]	22 ± 4.8	800 ± 120	3400 ± 170	3200 ± 250	2.2 ± 0.5
Concrete Storage[p]	130 ± 13	420 ± 34	--	--	2.1 ± 0.3

Table 4.2. Average concentration of dissolved reactive phosphorus (DRP) entering and exiting the ASTR-Hydrocyclone system.

	Deep-Pit Storage			Concrete Storage
	No Air, No $MgCl_2$ mg/L DRP as P	Air, No $MgCl_2$ mg/L DRP as P	Air and $MgCl_2$ mg/L DRP as P	Air and $MgCl_2$ mg/L DRP as P
In	25 ± 3.4	22 ± 1.7	22 ± 3.2	130 ± 13
Out	22 ± 2.3	21 ± 7.2	2 ± 0.4	11 ± 1.6
% Reduction	14%[+]	Not Significant[++]	91%[+++]	92%[+++]

TP Removal

Table 4.3 provides influent, ASTR effluent, hydrocyclone overflow (effluent and ASTR return), and hydrocyclone underflow TP concentrations, averaged across the three replications of each treatment in the deep-pit and concrete storage manure slurries. Hydrocyclone underflow TP concentrations were found to be significantly

[j] Dissolved Reactive Phosphorus. Standard Method 4500-P E (APHA, 1998)
[k] Total Phosphorus. Standard Method 965-17 (AOAC, 2002)
[l] Total Kjeldahl Nitrogen. Standard Method 2001-11 (AOAC, 2000)
[m] Ammonium Nitrogen. Standard Method 4500-NH_3 B & C for (APHA ,1998)
[n] Percent Total Solids. Standard Method 2540 B (APHA, 1998)
[o] Manure collected from a finishing facility employing a deep-pit under floor storage system near Ames, Iowa.
[p] Manure collected from a finishing facility employing a concrete storage system near Ames, Iowa.
[+] P-value = 0.0108
[++] P-value = 0.6968
[+++] P-value < 0.0001

higher than influent and effluent concentrations for all treatments in manure slurries from both the deep-pit and concrete storage systems (P< 0.0001).

Comparing underflow TP concentrations across treatments of manure slurry from the deep-pit storage found no significant difference between treatments without $MgCl_2$ addition. Introducing $MgCl_2$ with aeration provided a statistically significant increase in underflow TP concentration across treatments in manure slurry from deep-pit storage (P<0.0001).

Table 4.3. Total phosphorus concentrations (TP) of influent, air sparged tank reactor (ASTR) effluent, effluent, and hydrocyclone underflow.

	Deep-Pit Storage			Concrete Storage
	No Air, No Mg	Air, No Mg	Air and Mg	Air and Mg
	TP, mg P /kg	TP, mg P /kg	TP, mg P /kg	TP, mg P /kg
Influent	780 ± 140	930 ± 35	680 ± 150	420 ± 34
ASTR Effluent	900 ± 49	990 ± 30	860 ± 39	360 ± 79
Effluent	870 ± 60	900 ± 20	840 ± 58	350 ± 93
Hydrocyclone Underflow	1920 ± 370[AB]	2000 ± 390[AB]	2650 ± 668[B]	580 ± 47

The concentration of TP in the hydrocyclone underflow suggests that a portion of TP is being removed from the manure slurry. To identify the reduction of TP, the total mass of phosphorus was determined from measurements of influent and underflow mass flow rates and their corresponding TP concentrations. Table 4.4 provides the total mass of phosphorus entering the system and the total mass of

[A] No Significant Difference P = 0.3510, Treatment without aeration and without $MgCl_2$ vs. Treatment with aeration but without $MgCl_2$

[B] Significant Difference P < 0.0001, Treatment with aeration and $MgCl_2$ vs. Treatment without aeration and without $MgCl_2$; Treatment with aeration and $MgCl_2$ vs. Treatment with aeration but without $MgCl_2$

phosphorus removed from the system in the hydrocyclone underflow, averaged across replications for each treatment.

Results from the deep-pit manure tests show TP removal rates of 12% without the addition of $MgCl_2$ and without aeration, 14% with aeration but without $MgCl_2$ addition, and 9% with magnesium addition at 7.3:1 Mg^{2+}:PO_4^{3-} and aeration. Percent TP reductions between treatment of without $MgCl_2$ injection are not significantly different (P-value of 0.9373), however treatments without $MgCl_2$ injection have significantly higher TP reductions that treatment with $MgCl_2$ in the deep-pit manure slurry (no aeration-no Mg inject P-value = 0.0247, and aeration-no Mg inject P-value = 0.0222). Manure slurry from the concrete storage system had an 18% reduction in TP when treated with $MgCl_2$ addition at 1.6:1 Mg^{2+}:PO_4^{3-} and aeration. Results from treatments in the deep-pit manure slurry were not expected, as treatment with $MgCl_2$ injection provided lower TP removal rates than treatments without $MgCl_2$ injection; an examination of these results is provided in the discussion section.

Table 4.4. Total mass and percent reduction of total phosphorus (TP), averaged across replications for each treatment of the ASTR-hydrocyclone system

	Deep-Pit Storage			Concrete Storage
	No Air, No Mg TP, kg P	Air, No Mg TP, kg P	Air and Mg TP, kg P	Air and Mg TP, kg P
Influent	3.3 ± 1.4	5.5 ± 0.47	2.7 ± 1.1	1.7 ± 0.64
Hydrocyclone Underflow	0.40 ± .19	0.76 ± 0.34	0.25 ± 0.072	0.31 ± 0.039
% Reduction	12%	14%	9%	18%

X-ray Diffraction

Solids collected in the hydrocyclone underflow hopper from treatment with aeration and $MgCl_2$ were air dried and sieved prior to analysis with X-ray diffraction. The sieve analysis of solids recovered from they hydrocyclone is shown in Figure 4.5. X-ray diffraction results of sieve fractions passing 150 and 200 mesh (104 and 74 microns, respectively) were compared to the software database to identify crystalline species present (Figures 4.6 and 4.7). X-ray diffraction results indicate the presence of struvite, calcite, and quartz in the fraction passing 150 mesh and struvite, calcite, quartz, and dolomite in the fraction passing 200 mesh. The purity and amount of struvite formed was not quantified.

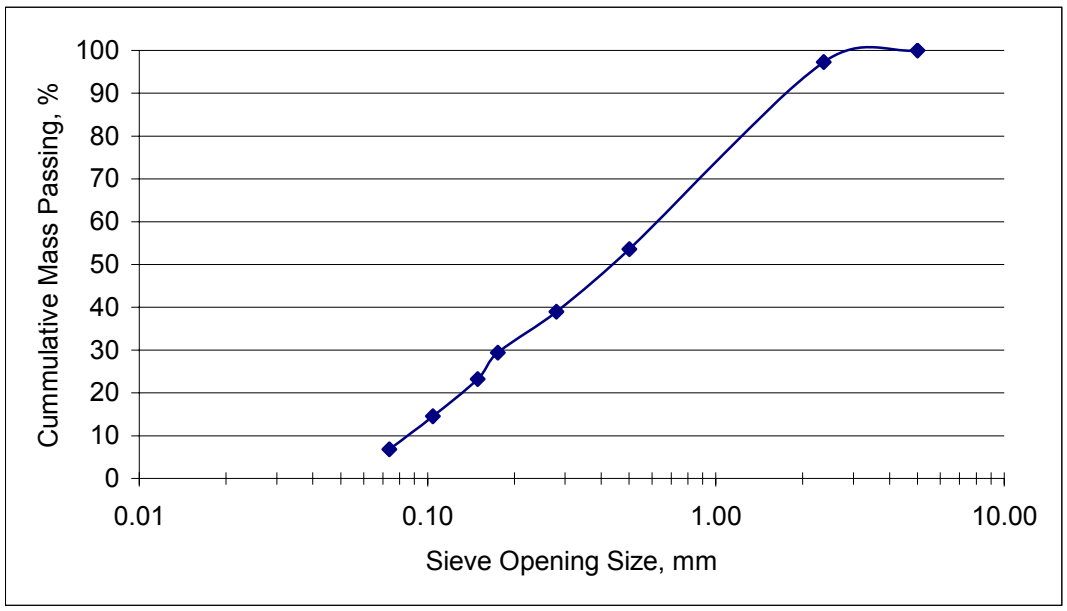

Figure 4.5. Sieve analysis of solids recovered from the hydrocyclone underflow for analysis of X-ray diffraction of ASTR-Hydrocyclone treated swine manure slurry

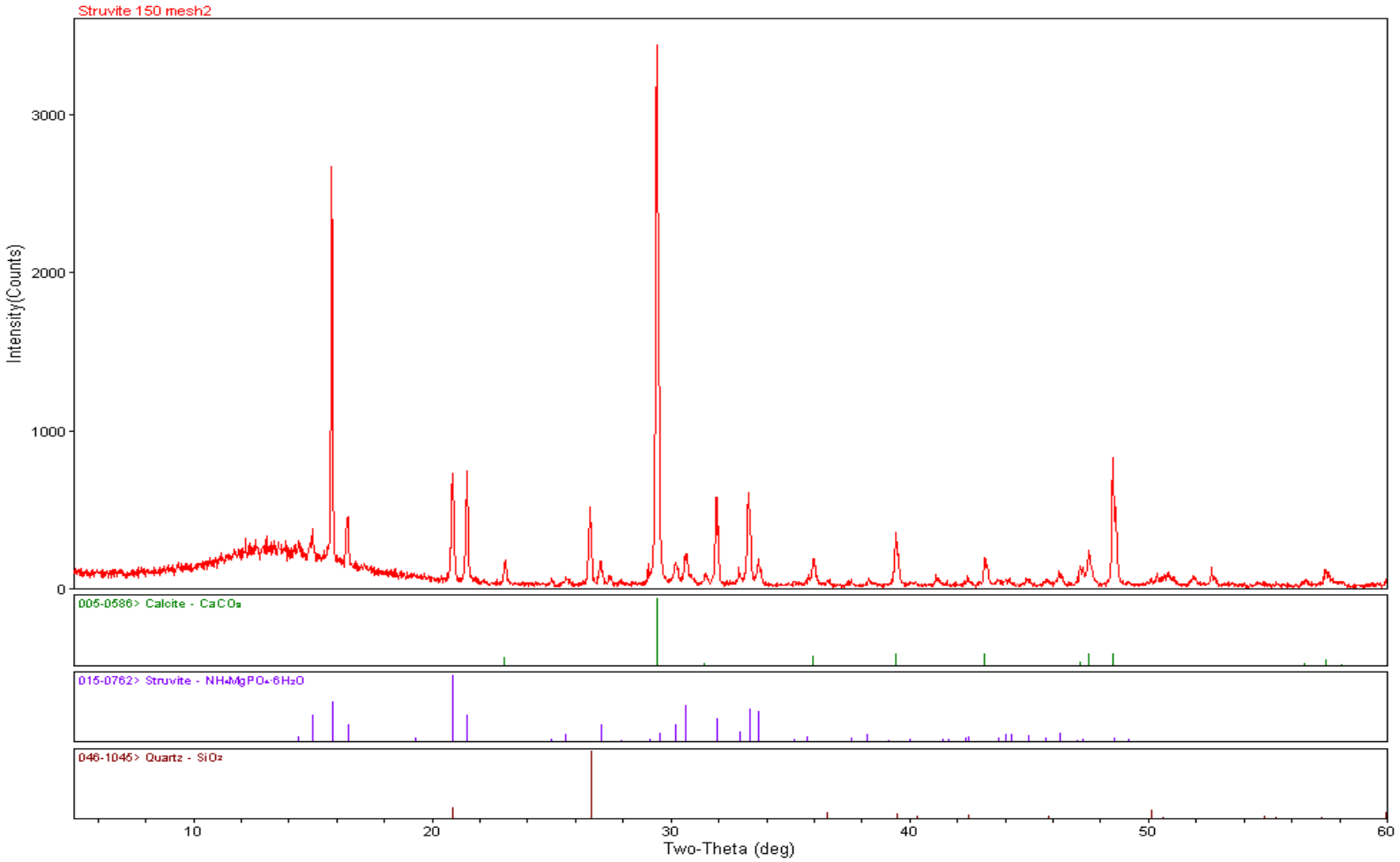

Figure 4.6. X-ray diffraction results of hydrocyclone solids passing a 150 mesh sieve showing correlating peaks of struvite, calcite, and quartz.

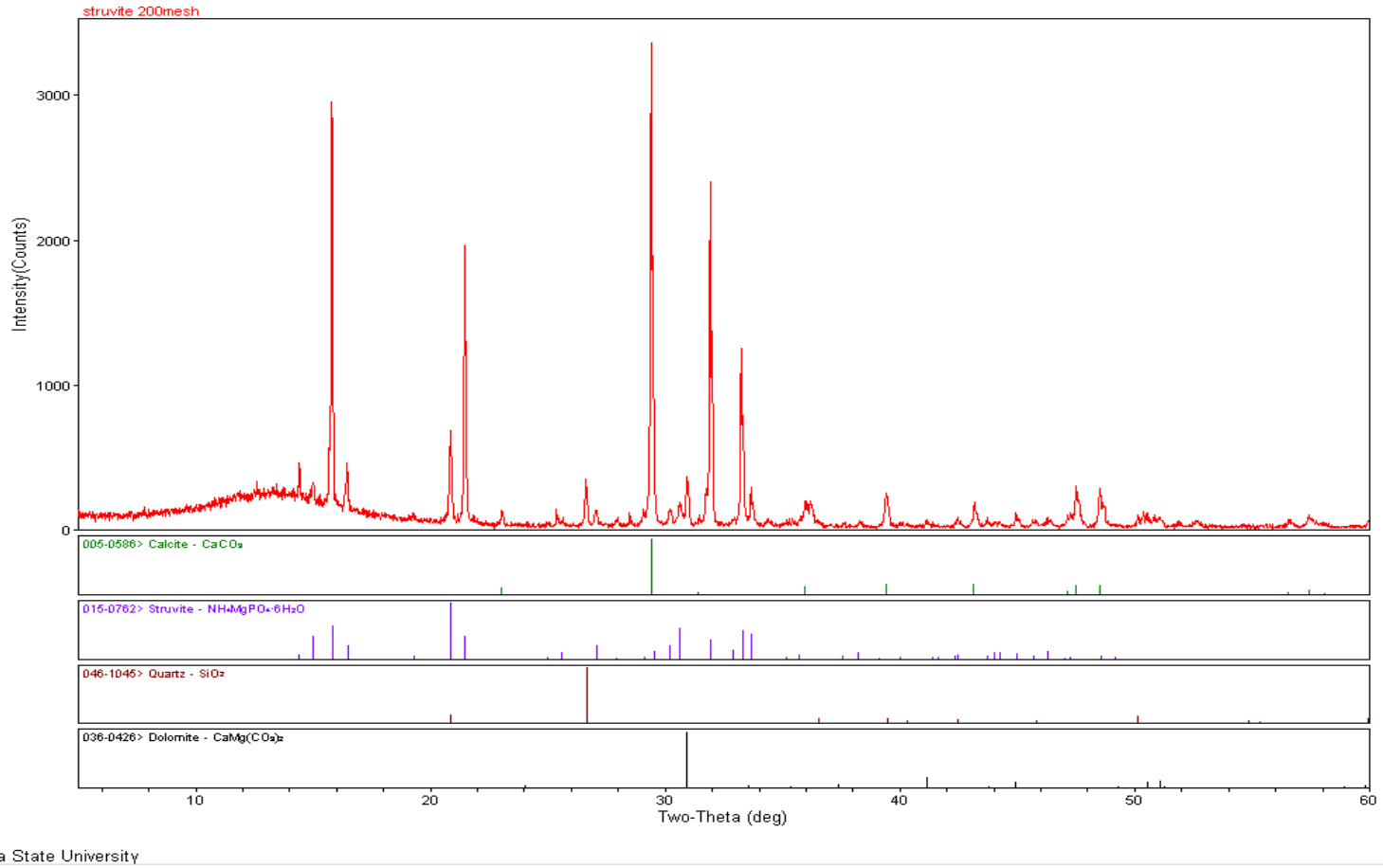

Figure 4.7. X-ray diffraction results of hydrocyclone solids passing a 200 mesh sieve showing correlating peaks of struvite, calcite, quarts, and dolomite.

Discussion

A continuous flow pilot-scale air sparged tank reactor (ASTR) was developed and tested for reducing dissolved reactive phosphorus (DRP) on manure slurries from two different storage systems (under-floor deep-pit and concrete storage). Effluent from the ASTR was processed through a McLanahan Model S1.506 A20 Hydrocyclone Separator (*McLanahan Corp.*, Hollidaysburg PA) for struvite-based phosphorus recovery. The ASTR-hydrocyclone system was initially tested on manure slurry from a deep-pit storage system at a flow rate of 115 L/min (31 gpm) with a 16-minute HRT with three treatments, performed in triplicate: 1) ASTR-hydrocyclone without aeration or $MgCl_2$ injection, 2) ASTR-hydrocyclone with aeration, but no $MgCl_2$ injection, and 3) ASTR-hydrocyclone with aeration and $MgCl_2$ injection. Due the low fraction of TP available as DRP (3%) in the deep-pit manure slurry, the ASTR-hydrocyclone system was tested on manure slurry from a concrete storage system which had 31% of the TP available as DRP for struvite precipitation. Manure slurry from the concrete storage was tested only with aeration and $MgCl_2$ injection, as results from treatment without $MgCl_2$ injection in the deep-pit slurry did not provide sufficient DRP reductions for struvite-based phosphorus removal.

Dissolved Reactive Phosphorus Reduction

The ASTR-Hydrocyclone system reduced the DRP concentration by 91% in the deep-pit manure slurry when air sparging proceeded at 566 L/min and $MgCl_2$ was applied at a Mg^{2+}:PO_4^{3-} ratio of 7.3:1. The average influent DRP concentration of 22.2 mg P/L was reduced to an average effluent DRP concentration of 2.0 mg P/L. Dissolved reactive phosphorus was reduced from 130 mg P/L to 11 mg P/L in

manure from the concrete storage system; the 92% reduction was achieved with aeration at 566 L/min and $MgCl_2$ injection at a Mg^{2+}:PO_4^{3-} ratio of 1.6:1.

Effluent from the treatment of the deep-pit manure slurry had a significantly lower DRP concentration than the effluent of from the treatment of the concrete storage manure slurry (P-value < 0.0005). This difference may be attributed to the higher struvite conditional solubility product created by over application of magnesium during the deep-pit manure treatment and the lower operational pH during the concrete storage manure treatment.

X-ray diffraction and sieve analysis of effluent from the hydrocyclone underflow indicates that struvite is being formed as fine particles (<104 microns) in the ASTR-hydrocyclone system. Results indicate that the ASTR-Hydrocyclone system is capable of effectively and significantly reducing DRP at high treatment flow rates when aeration and $MgCl_2$ is applied. Further testing is needed to identify the optimal HRT's, magnesium injection rates, and pH requirements which provide adequate treatment levels and minimize capital and chemicals costs.

Total Phosphorus Removal and Recovery via Struvite Precipitation

The maximum amount of struvite-based phosphorus removal and recovery is related to the availability of phosphorus as DRP. The ratio of DRP:TP allows for the identification of maximum theoretical TP removal rates. Manures with 1:2 DRP:TP ratios can provide up to 50% TP removal via struvite precipitation and recovery. Manure slurry from the deep-pit storage system had an approximate DRP:TP ratio of 1:36 (22 mg P/L : 800 mg P/L), indicating only 3% of TP can be removed through struvite precipitation and recovery. Manure slurry from the concrete storage system

had an approximate DRP:TP ratio of 1:3 (130 mg P/L : 420 mg P/L), indicating 31% of TP could be removed through struvite precipitation and recovery.

A typical corn crop in Iowa requires 0.50 – 0.54 kg N/25 kg of grain produced (1.1 to1.2 lb N/bu) and 0.17 kg P_2O_5/25 kg of grain produced (0.375 lb P_2O_5/bu) (Iowa State University, University Extension, 2003). This suggests that manure slurries should have a N:P_2O_5 ratio of 3:1 for land application at a rate which balances both N and P for a typical Iowa corn crop. Manure slurry from the deep-pit system had an initial N:P_2O_5 ratio of 1.9:1; if applied at nitrogen levels for a typical corn crop in Iowa, phosphorus would be applied in excess.

To determine achievable treatment levels of struvite-based DRP reduction and recovery for TP removal in a specific manure slurry, the relationship between the DRP:TP, N:P_2O_5, and the combined efficiency of DRP reduction and recovery should be considered.

Figure 4.6 illustrates the achievable N:P_2O_5 ratio dependant upon the DRP:TP ratio and combined DRP reduction and recovery efficiencies for a manure slurry similar to that used in this study with an initial N:P_2O_5 ratio of 1.9:1. For example, treatment with the ASTR has the potential to adjust the N:P_2O_5 ratio to 2.0:1 based on the DRP:TP limit of the deep-pit manrue. To achieve the desired (balanced) N:P_2O_5 ratio of 3:1, manure slurry from this specific system would require at least 38% of the TP to be in the form of DRP for the precipitation and recovery of struvite, assuming 100% DRP reduction and removal efficiency.

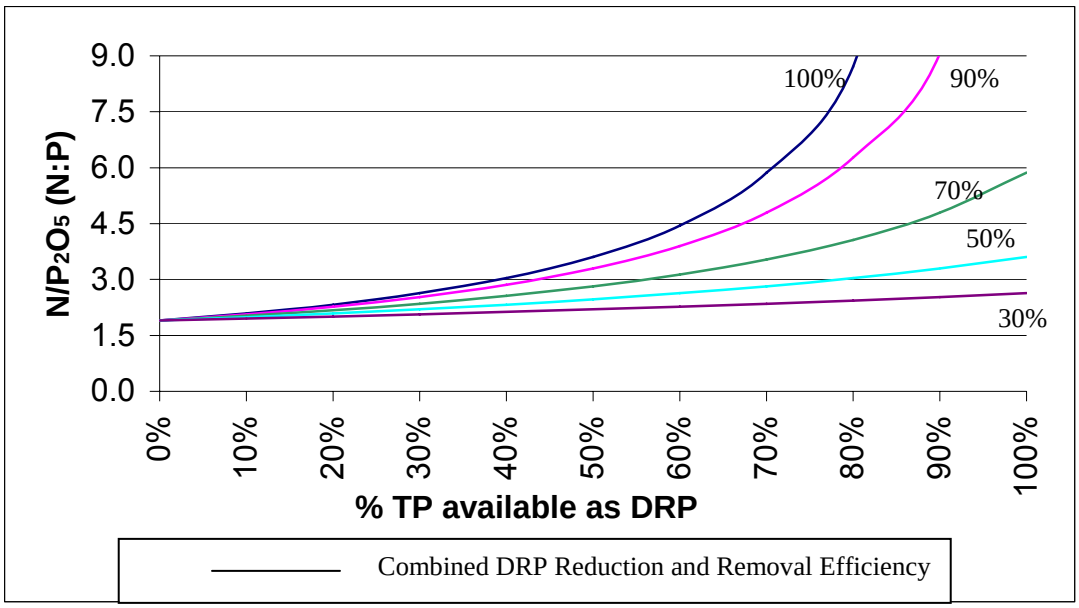

Figure 4.6. Achievable $N:P_2O_5$ ratio dependant upon the DRP:TP ratio and combined DRP reduction and recovery efficiencies for a manure with an initial $N:P_2O_5$ ratio (1.9:1)[q]

Decreasing the DRP reduction and removal efficiency, necessitates a higher percentage of TP to be in the form of DRP to achieve the desired $N:P_2O_5$ ratio of 3:1. Testing of the ASTR system at bench and pilot-scale indicated that a 90% reduction in DRP is achievable with a $Mg:PO_4$ ratio of at least 1.6:1. While the ASTR-hydrocyclone did not show a significant reduction in TP, an estimate of the required DRP reduction and removal efficiency can be identified from Figure 4.6 for a specific DRP:TP ratio (and visa-versa). For example, if a treatment system provided a DRP reduction and removal efficiency of 70%, the manure slurry from the deep-pit system

[q] Source: Ames, IA deep-pit production facility (utilized in this study)

would require approximately 55% of the TP to be available as DRP to achieve the desired $N:P_2O_5$ ratio of 3:1.

The initial $N:P_2O_5$ ratio of the manure slurry also plays a significant role in determining the required DRP reduction and removal efficiency and DRP:TP ratio to provide the desired treatment level. To show this relationship, three initial $N:P_2O_5$ ratios where identified to represent typical Iowa deep-pit facilities (Table 4.5). Figure 4.7 shows the relationship between the achievable $N:P_2O_5$ ratio vs. DRP:TP ratio, assuming a 70% DRP reduction and removal efficiency. For example manure slurry with an initial $N:P_2O_5$ ratio of 1.9:1 would require approximately 55% of the TP to be available as DRP to achieve an effluent $N:P_2O_5$ ratio of 3:1. A manure slurry with a lower initial $N:P_2O_5$ ratio of 1.25:1 would require approximately 90% of the TP to be available as DRP to achieve the same treatment level with struvite-based phosphorus removal.

Table 4.5. Initial Nitrogen to Phosphorus ratios ($N:P_2O_5$) of swine manure slurries representing typical Iowa deep-pit finishing facilities.

$N:P_2O_5$ ratio	$N:P_2O_5$ ratio	Source
High	1.90:1	Ames, IA Producer (utilized in this study)
Medium	1.40:1	Nutrient content of finishing pig manure as excreted (MWPS 1993)
Low	1.25:1	Manning, IA Producer (independent lab analysis)

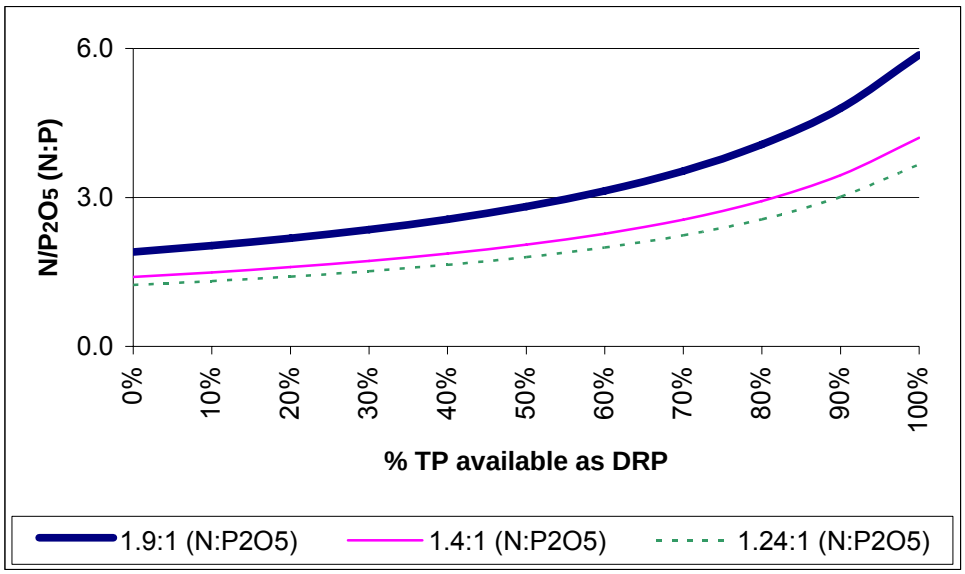

Figure 4.7. Achievable $N:P_2O_5$ ratio vs. DRP:TP ratio, assuming a 70% DRP reduction and removal efficiency.

Hydrocyclone Separation for Phosphorus Removal

Results from the deep-pit manure tests show TP removal rates of 12% without the addition of $MgCl_2$ and without aeration, 14% with aeration but without $MgCl_2$ addition, and 9% with magnesium addition at 7.3:1 $Mg^{2+}:PO_4^{3-}$ and aeration. Manure slurry from the concrete storage system had an 18% reduction in TP when treated with magnesium addition at 1.6:1 $Mg^{2+}:PO_4^{3-}$ and aeration.

Finding higher TP reduction rates in treatments without $MgCl_2$ injection in comparison to treatment with MgCl2 in the deep-pit manure was not expected. The precipitation of struvite from $MgCl_2$ injection should theoretically provide higher TP reduction rates due to the separation struvite by the hydrocyclone. However, the low availability of TP as DRP for struvite precipitation (3%) in the deep-pit manure slurry

suggests that treatment with $MgCl_2$ injection will have a small impact on TP recovery and may not be identifiable due to the variability between samples collected for analysis. All treatments of the deep-pit manure slurry exceeded the theoretical struvite-based phosphorus removal rate. The reduction of TP without an associated reduction of DRP indicates that prior to treatment, a portion of TP in the manure slurry was in the form of dense solids, most likely undigested feed or calcium-phosphorus precipitates, dense enough to be separated by the hydrocyclone. The difference in TP reduction performance between treatments in the deep-pit manure slurry is most likely due to TP variability and its impact on the collection of representative samples for analysis.

Theoretical predictions of struvite-based phosphorus removal from the concrete storage manure slurry provide a maximum TP reduction rate of 31%. Treatment of manure from the concrete storage system provided phosphorus removal rates lower than the theoretical struvite-based TP reduction. This indicates that the hydrocyclone was not able to capture all precipitated struvite particles. Hydrocyclone recovery efficiency is dependant on the particle size and density as well as liquid characteristics. Factors which may reduce struvite removal efficiency with a hydrocyclone include: precipitation of struvite particles too small to be captured, struvite precipitation onto particles with low densities such as organic matter, and hindered settling of struvite particles by low density solids.

Assuming that struvite was the sole contributor to TP in hydrocyclone underflow, the system achieved a combined TP reduction and removal efficiency of 58% in the manure slurry from the concrete storage system. However, results from

the deep-pit system indicated separation of TP without struvite precipitation, therefore the struvite reduction and removal efficiency was likely less than 58%.

X-ray diffraction analysis of material passing the 150 mesh (104 microns) indicated the presence of struvite, calcite ($CaCO_3$), and quartz (SiO_2). X-ray diffraction analysis of materials passing the 200 mesh (74 microns) indicated the presence of struvite, calcite, quartz, and dolomite ($CaMg(CO_3)_2$). The presence of quartz indicates sand, most likely introduced to the system through dust, dirt, and construction materials. Calcite is a sparingly soluble solid (K_{sp} of $10^{-8.34}$), and is common in water systems with high alkalinity (Snoeyink and Jenkins, 1980). In Iowa, groundwater is typically classified with high alkalinity levels due to the presence of calcium and magnesium hardness. The presence of Mg^{2+} has been shown to inhibit the growth of calcite (Morse, 1983). Therefore, calcite was most likely present prior to treatment with the ASTR-Hydrocyclone system. Dolomite is a calcium-magnesium complex with a slow precipitation rate (Mamais et at, 1994). Calcium-magnesium carbonate species precipitate in solutions with high magnesium concentrations or from the supernatants of anaerobic sludge digesters (Snoeyink and Jenkins, 1980); therefore it is possible that dolomite was present prior to treatment or precipitated due to the over application of $MgCl_2$ during treatment.

Specific gravity of crystalline species found in the underflow solids are shown in Table 4.6. Quartz, dolomite, and calcite have significantly higher specific gravities than struvite. If we are capable of capturing a specific size of struvite particles with hydrocyclone separation, we will also capture materials of equal size which have higher specific gravities.

Table 4.6. Specific gravities of crystalline materials identified by X-ray diffraction in sieved hydrocyclone underflow solids.

	Struvite	Quartz	Calcite	Dolomite
Specific Gravity	1.7	2.65	2.72	2.85

Further testing should be performed on manure slurries better suited for struvite precipitation and the hydrocyclone should be tested under various operational flow rates and pressure drops to identify the optimal settings for struvite recovery and TP removal from typical manure management systems. Alternative methods to separate struvite from ASTR-treated manure slurries should also be investigated.

ASTR-Hydrocyclone Treatment Economics

Operational and capital costs associated with implementing the ASTR-hydrocyclone system were evaluated to provide insight into the economic feasibility of struvite-based phosphorus recovery. Table 4.7 provides an estimate of the pilot-scale ASTR-Hydrocyclone capital cost (Base Cost) and predictions of full-scale ASTR-hydrocyclone capital cost. Scaling equipment components from base cost to predicted cost was accomplished with Equation 4.3. Each equipment component was scaled from defined pilot-scale size parameters (volume, flow rate, horsepower) to the required size for a full-scale system. For example, the full-scale cost of the reactor tank equals the cost of the pilot-scale tank times the ratio of the required full-scale volume to the volume of the pilot-scale tank to the power of the economy of scale sizing exponent of reactor tanks provided in Table 4.7.

Equation 4.2. $$Cost_{FullScale} = Cost_{PiloScale}\left[\frac{Size_{FullScale}}{Size_{PilotScale}}\right]^{n}$$

where: n *= economy of scale sizing exponent* (Brown, 2003)

Economies of scale associated with the amount of manure treated annually provide incentive for an ASTR-Hydrocyclone system to be operated as a mobile treatment system by a custom manure applicator or cooperative. Assuming the annual treatment capacity allows the interest and depreciation of the full-scale capital cost to be associated into the operational costs on a per unit treatment base. Furthermore, a selling price of the service can be defined to provide the custom manure applicator or cooperative to achieve an expected return on investment.

The operating costs included in analysis were direct costs of energy and chemical consumption and indirect costs of interest, depreciation, and selling price. Operational cost of the full-scale system was assessed at a continuous flow rate of 5700 L/min (1500 gal/min), assuming the annual treatment capacity to be 450 million L/year (119 million gallons/ year). Indirect costs of annual interest were set 6% for a 10-year loan, a 10% straight-line depreciation was assumed over the useful life of 10 years, and selling price of the treatment service was set to achieve a 10% return on investment. Fuel consumption to operate the full-scale system was estimated to be 17 L/h, the cost of diesel fuel used was \$0.91/L (*Energy Information Administration*, 27 November 2007). The market price for bulk $MgCl_2$ used was \$0.95/kg Mg^{2+} (*Hydrite Chemical Co.*, Iowa).

Table 4.7. Capitol cost and unit cost of the pilot-scale ASTR-Hydrocyclone and predicted cost of full-scale ASTR-Hydrocyclone systems

Pilot Scale Unit, 190 L/min (50 gal/min)				Predicted Full Scale Cost	
Equipment	Size	Base Cost	n, Sizing Exponent	1900 L/min	5700 L/min
Intake Pump	200 L/min	$ 3,800	0.52[r]	$ 12,252	$ 22,279
Hydro Pump	750 L/min	$ 8,000	0.52[q]	$ 12,972	$ 26,490
Hydrocyclone	550 L/min	$ 6,000	1[q]	$ 20,727	$ 62,182
Tank	3780 L	$ 1,800	0.3[q]	$ 3,591	$ 4,994
Trailer	22,000 kg	$ 2,900	0.92[s]	$ 24,000	$ 65,784
Generator	15 kW	$ 2,200	0.75[q]	$ 12,372	$ 28,201
Compressor	566 L/min	$ 1,000	0.75[q]	$ 5,623	$ 12,819
Magnesium Pump	850 W	$ 800	0[t]	$ 800	$ 800
Influent Flow Meter	2"	$ 2,850	0.05[u]	$ 3,196	$ 3,375
Effluent Flow Meter	4"	$ 2,950	0.05[t]	$ 3,308	$ 3,494
Air Flow Meter		$ 700	0[s]	$ 700	$ 700
Underflow Mass		$ 500	0[s]	$ 500	$ 500
Total Equipment		$ 33,500		$ 100,042	$ 231,617
Construction Materials		$ 10,000		$ 23,010[v]	$ 53,272[u]
Total Base	**190 L/min**	**$ 43,500**		**$ 123,051**	**$ 284,889**
Base Cost per Treatment Capacity	L/min	$ 229		$ 65	$ 50

Energy cost for the full-scale ASTR-hydrocyclone system was estimated to be $0.0452/1000L manure slurry treated ($0.172/1000 gal). The chemical cost associated with treatment is directly proportional to the amount of phosphorus reduction required. Higher TP removal rates require larger chemical amendments

[r] Source: Brown, 2003
[s] Source: *Mid-State Utility Trailers*, Omaha NE
[t] Assumed to have zero scale due to low flow rates
[u] Calculated from difference in price and capacity of purchased units

which increases the operational cost, Equation 4.1 calculates the chemical cost dependant upon the required reduction of total phosphorus. Table 4.8 provides a summary of total operating cost of treatment, due to the variations of chemical requirements for different hog production facilities, the chemical cost is associated as a variable dependant upon the required phosphorus removal rate. Equation 4.2 is an estimate of the total cost per 1000L of deep-pit manure treated by a custom applicator or cooperative. A case study of a typical deep-pit finishing facility in Iowa is presented below to evaluate the system economics of struvite-based phosphorus removal.

Equation 4.1. $$Cost_{Chemical} = 0.0127\left[TP_{removal}\right]$$

where: $Cost_{Chemical}$ = *Magnesium Chloride Cost, $/1000 L slurry treated*

$TP_{removal}$ = *Required reduction of total phosphorus, mg P/L*

[v] Based on 23% of total cost required for materials to build pilot-scale unit

Table 4.8 Summary of operating costs for a full-scale ASTR-hydrocyclone system treating 450 million L of manure slurry per year at a flow rate of 4700 L/min.

Capital Cost	$	285,000	450 million L/year capacity

	Cost, $/1000L	Description
FIXED COST		
Direct		
Fuel	$ 0.0452	Cost of diesel fuel $0.91/L
Indirect		
Capital Charge	$ 0.0860	6% interest for 10 years on total capital cost
Depreciation	$ 0.0633	10% straight line depreciation of total capital
VARIABLE COST		
Chemical	$ 0.0127[$TP_{Removal}$]	From Equation 4.1
TOTAL COST Operating	$ 0.0127[$TP_{Removal}$] + 0.1946	
CUSTOM CHARGE	$ 0.0127[$TP_{Removal}$] + 0.2140	10% gross return on investment

Equation 4.2. $$Cost_{Custom} = 0.0127\left[TP_{removal}\right] + 0.214$$

where: $Cost_{Custom}$ = *Custom applicator charge, $/1000 L slurry treated*

$TP_{removal}$ = *Required reduction of total phosphorus, mg P/L*

Case Study

Values used in this case study are intended represent a typical Iowa deep-pit pork production facility. A 10,000 head/year deep-pit pork production facility near Manning, IA produces approximately 6.0 million Liters of manure slurry per year (1.6 million gallons/year). An independent lab analysis indicates that the slurry contains 5.31 kg N/1000L and 2.82 kg P_2O_5/1000L (25.8 lb N/1000gal and 23.5 lb P_2O_5/1000gal). Based on crop nutrient requirements and facility information,

approximately 430 acres of corn is needed for manure slurry application at nitrogen levels. Assuming that the producer has no additional land and cannot economically export the liquid manure, if regulations require the application of the swine manure slurry based on phosphorus levels, the producer must reduce the phosphorus generated by the facility or remove phosphorus prior to land application.

To comply with phosphorus based application regulations, the producer could reduce the number of pigs fed per year from 10,000 to approximately 6,400 (36% reduction). Furthermore, applying the manure slurry at phosphorus levels creates a nitrogen deficit of approximately 11,400 kg N/yr (25,000 lb N/yr). This requires an additional application of commercial nitrogen fertilizer to maintain corn yields, at a yearly fertilizer cost of $6,400 (Anhydrous ammonia $510/ton, *Heartland Coop*, Slater, IA, Fall 2007).

Assuming that a custom applicator or cooperative operates a mobile struvite-based treatment system with a DRP reduction efficiency of 90% and removal efficiency 80% (combined DRP removal and recovery efficiency of 72%), the number of pigs which can be placed back into the production facility can be determined. If 50% of the TP is available as DRP for struvite precipitation, treatment would allow the production facility to feed approximately 10,000 pigs per year. Furthermore, treatment would recover approximately 6,140 kg P_2O_5/year (13,500 lb P_2O_5/year). Liquid swine manure is typically sold at 70% of their nutrient value, assuming that the separated solids can be sold for 70% of the commercial phosphate value, a revenue of $2,300/year could be realized (Phosphate $495/ton, *Heartland Coop*, Slater, IA, Fall 2007).

Based on the economical analysis of the full-scale ASTR-hydrocyclone system, avoidance of commercial nitrogen fertilizer, and sale of separated phosphorus, the yearly cost of treatment would be approximately $222,000. For this case study, to offset the cost of treatment, a profit of at least $61.66/pig replaced would be required. For the entire 10,000 head production facility, the annual cost equates to $22.20/pig space or $0.0353/L of deep-pit manure slurry treated ($0.134/gal).

Custom feeding operations are contracted by large producers to finish pigs to market weight. The average custom feeding operation in western Iowa is paid $13.50 per finished pig for operational management, facilities, utilities, labor, and manure management (personal correspondent with a custom feeding operation near Manning, IA). This indicates that struvite-based phosphorus removal system tested is not currently economically viable for deep-pit hog production.

Conclusion

Field experiments with the ASTR-Hydrocyclone treatment system demonstrated that it was possible to significantly reduce the quantity of dissolved reactive phosphorus (DRP) in swine manure slurry when aeration and $MgCl_2$ were provided. Average DRP reductions of 91% were observed at continuous flow treatment rates of 115 L/min (31 gal/min), producing an effluent with an average DRP concentration of 2 mg P/L in manure slurry from deep-pit storage. Average DRP reductions of 92% were observed at continuous flow treatment rates of 80 L/min (21 gal/min), producing an effluent with an average DRP concentration of 11 mg P/L in manure slurry from a concrete storage system.

A hydrocyclone separator was implemented to provide struvite-based total phosphorus (TP) reductions. The ASTR-hydrocyclone system provided TP removal rates of 9% to 14% in manure slurry from deep-pit storage and 18% in manure slurry from a concrete storage system. Comparisons of ASTR-hydrocyclone treatments and theoretical struvite-based TP removal rates versus actual TP removal rates indicate that the hydrocyclone did not provide sufficient struvite separation efficiencies as operated. Analysis of struvite precipitation efficiency and required phosphorus reduction levels in typical deep-pit manure slurries indicates that a feasible separation system should provide struvite removal efficiency of 70% to 80%. X-ray diffraction of solids collected from the underflow of the hydrocyclone indicated the presence of struvite as small particles. The quantity and purity of struvite collected was not determined. Further research should focus developing an alternative method to remove struvite from ASTR treated manure slurries.

Prior to the application of struvite-based phosphorus recovery, manures should first be analyzed to determine if treatment can provide the desired phosphorus reduction levels. Achievable treatment levels of struvite-based DRP reduction and recovery for TP removal in a specific manure slurry is dependant on the relationship between the DRP:TP, N:P_2O_5, and the combined efficiency of DRP reduction and recovery. Manure slurries with high DRP:TP ratios have the potential to provide significant TP reductions dependant upon the initial N:P_2O_5 ratio and degree of separation efficiency required to achieve a manure slurry balanced in terms of N and P for a specific crop. Further testing of the ASTR-Hydrocyclone

system should be performed on manure slurries with significant portions (>30%) of TP available as DRP for precipitation as struvite.

An analysis of chemical, energy, capital, and depreciation operational costs for a full-scale (4700 L/min) ASTR-hydrocyclone unit indicated a high dependence on phosphorus removal requirements. The chemical cost of magnesium amendment is directly related DRP reduction needed to achieve the desired treatment level. A case study of a typical Iowa deep-pit pork production facility feeding 10,000 head/year, could implement struvite-based phosphorus removal with an ASTR-separation system for an approximate yearly cost of $222,000. This annual cost equates to $22.20/pig space or $0.0353/L of deep-pit manure slurry treated ($ 0.134/gal) and indicates that the struvite-based phosphorus removal system tested in deep-pit swine manure is not economically viable.

Acknowledgements

This project is funded by a grant from the USDA NRI contract number 20033550415627.

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CHAPTER 5

GENERAL CONCLUSIONS

Struvite precipitation is a technically feasible method capable of reducing dissolved reactive phosphorus (DRP) allowing for total phosphorus (TP) removal and recovery from swine manure slurries. Point of treatment considerations within modern pork production facilities indicate that the most feasible struvite treatment scheme should be implemented during land-application events; necessitating a treatment system capable of operating at high flow rates.

Bench-scale and pilot-scale continuous flow air sparged tank reactors (ASTR), incorporating aeration and $MgCl_2$ injection, provided and maintained significant reductions of dissolved reactive phosphorus in swine manure slurries (78% and 95% bench-scale, 91% and 92% pilot-scale). The pilot-scale ASTR was capable of effectively and reliably reducing DRP from swine manure slurries at an average flow rate of 80 to 115 L/min.

Dissolve phosphorus reduction performance utilizing manures slurries collected from four different manure management systems (two at bench-scale and two at pilot-scale) indicates that the simple design provides a flexible system for application at various full-scale operations. The well defined sizing criteria of the ASTR allows for the design of a full-scale system which could be an effective method to precipitate struvite at high flow rates required for application to existing modern pork production facilities. However, achieving TP reduction with the ASTR

requires a downstream separation system capable of effectively and efficiently removing precipitated struvite.

A hydrocyclone separator was implemented to provide struvite-based total phosphorus (TP) reductions from ASTR treated manure slurries. X-ray diffraction of solids collected from the underflow of the hydrocyclone indicated the presence of struvite. Comparisons of ASTR-hydrocyclone treatments and theoretical struvite-based TP removal rates versus actual TP removal rates indicate that the hydrocyclone does not provide sufficient TP separation efficiency as operated.

Selection of Manures Suitable for TP Reduction via Struvite Precipitation

Achievable treatment levels of struvite-based DRP reduction and recovery for TP removal in a specific manure slurry is dependant on the relationship between the DRP:TP, N:P_2O_5, and the combined efficiency of DRP reduction and recovery. Manure slurries with high DRP:TP may have significant TP reductions with a effective and efficient separation system, providing the opportunity to balance the manure for N and P crop requirements.

Prior to the application of struvite-based phosphorus recovery, manures should first be analyzed to determine if treatment can provide the desired phosphorus reduction. By adjusting $MgCl_2$ amendment rates, a predetermined fraction of DRP can be precipitated as struvite for recovery, allowing site-specific treatment capable of producing a manure slurry fertilizer, which is balanced to meet crop requirement in terms of N and P nutrients.

Magnesium Demand Determination

Determining the real-time magnesium demand for a specific reduction of DRP via struvite precipitation is essential for the application of an economically viable struvite precipitation system. Laboratory experiments with several manures indicated that monitoring solution conductivity during struvite precipitation does not provide an indication of reaction completion. Current methods to directly monitor the availability of magnesium, ammonium, and phosphate are not technically or economically viable for implementation in on-farm treatment systems.

Pilot-scale Economics

An analysis of chemical, energy, capital, and depreciation operational costs for a full-scale (4700 L/min) ASTR-hydrocyclone unit indicated a high dependence on phosphorus removal requirements. A case study of a typical Iowa deep-pit pork production facility feeding 10,000 head/year, could implement struvite-based phosphorus removal with an ASTR-seperation system for an approximate yearly cost of $222,000.The capital cost of the pilot-scale ASTR-hydrocyclone was calculated to be $43,500, providing a per unit treatment cost of $229/ L/min. Estimations of the capital cost for full-scale units (1900 L/min and 5700 L/min) indicates a total capital cost of $123,000 and $285,000, respectively; full-scale capital costs on a per unit treatment base are estimated to be $65/ L/min and $50/ L/min, respectively.

Recommended Future Research

- Optimization of the ASTR, accounting for economics vs. degree of treatment by determining:

  - Minimum requirements for hydraulic retention time HRT
  - Required pH adjustment level
  - Required magnesium demand
- Modifications to the ASTR system
  - Incorporation of automated flow monitoring
  - Implementation of a caustic amendment system to provide supplemental pH adjustment when aeration alone is not adequate
- Identification of a viable separation system to remove struvite from ASTR-treated manure slurries
- Focused investigations of hydrocyclone operational conditions to identify the effect of applied gravitational force on:
  - Overall struvite removal efficiency
  - Recoverable struvite particle size
  - Overall nutrient content and value of recovered solids
- Modification of the hydrocyclone solids separator to operate as a traditional hydrocyclone.
- Further testing of the ASTR-Hydrocyclone system should be performed to identify optimal operational conditions and hydrocyclone separation efficiencies in manures with:
  - Significant portions of TP available as DRP for precipitation as struvite (>30%).

  - Low and high solids content due to variations in manure management practices (deep-pit, covered storage tanks, open storage tanks)

- Dewatering, processing, and handling of separated solids
- Development of a phosphate ion selective electrode (ISE) that is capable of withstanding the harsh environment of manure to monitor the magnesium demand for struvite precipitation in real-time.
- Development of a dedicated economic model evaluating struvite-based phosphorus removal
  - Capital investment vs. treatment capacity
  - Economies of scale based on total yearly treatment
  - Operational costs associated with
    - Chemical and energy requirements
    - Depreciation, maintenance, and labor
    - Combined removal and separation efficiency
  - Cost reductions associated with
    - Reduced magnesium and chemical dependence
    - Reduced land application requirements
    - Transportation or pumping of liquids off-farm
    - Reduced field operations and direct cost of supplemental commercial fertilizer application

- Value of recovered solids